OFFICE OF
RIVER PROTECTION
United States Department of Energy

DISTINCTIVE 3rd Annual Meeting
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Hanford; The Creation and Remediation of the Legacy

ORP-60691

Presented by: Albert A. Kruger, Glass Scientist, US Department of Energy

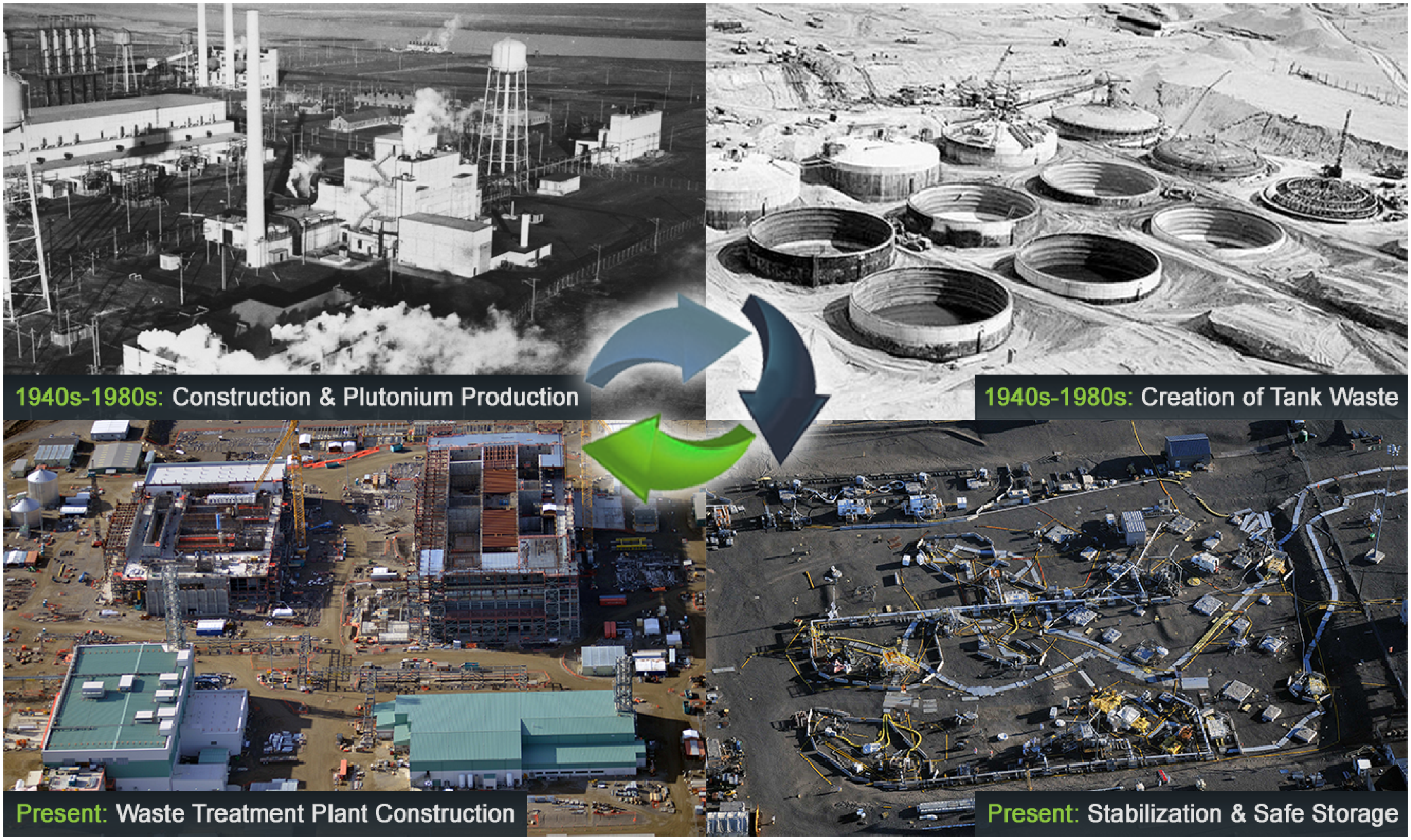
Presentation Outline & Key Messages

- Background, Hanford Waste Generation
- Challenges and Approaches for Hanford Vitrification
- Advanced LAW glass formulations allow the additional flexibility to reconsider feed vectors to the WTP.
- Performance enhancements through improved glass formulations are essentially transparent to the engineered facility.
- Next Steps

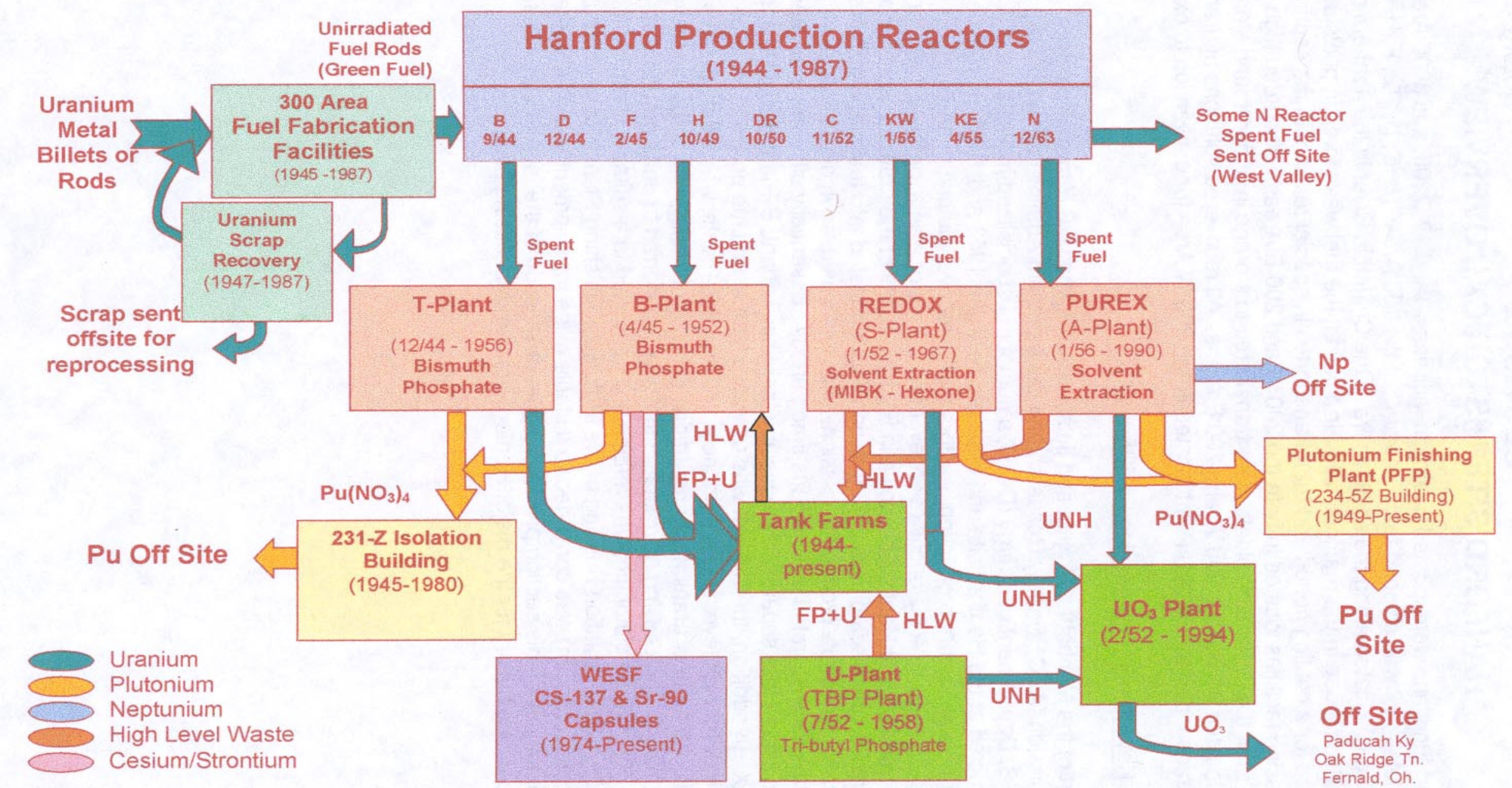
Background

- **1943-1964: 149 single-shell tanks constructed**
  - 67 presumed to have leaked
- **1968-1986: 28 double-shell tanks constructed**
  - 1 leaking, waste contained within annulus

Historical Overview of the Hanford Site



Generation of Hanford Tank Wastes

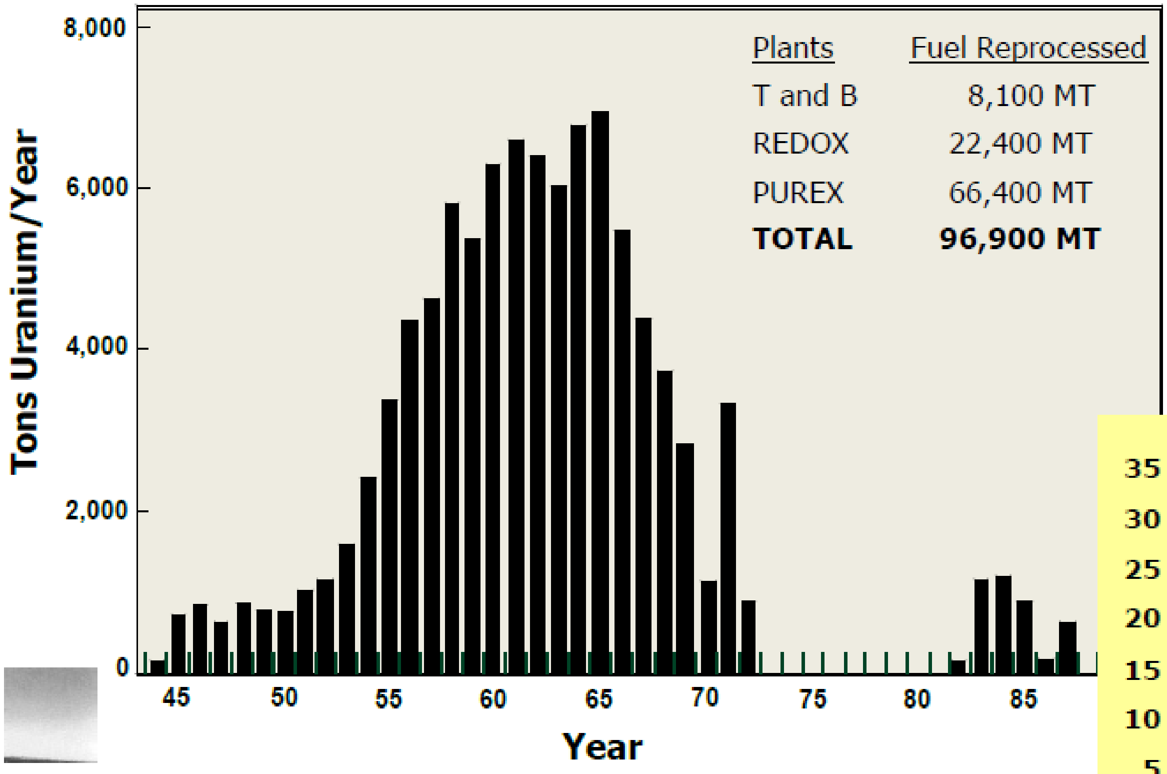


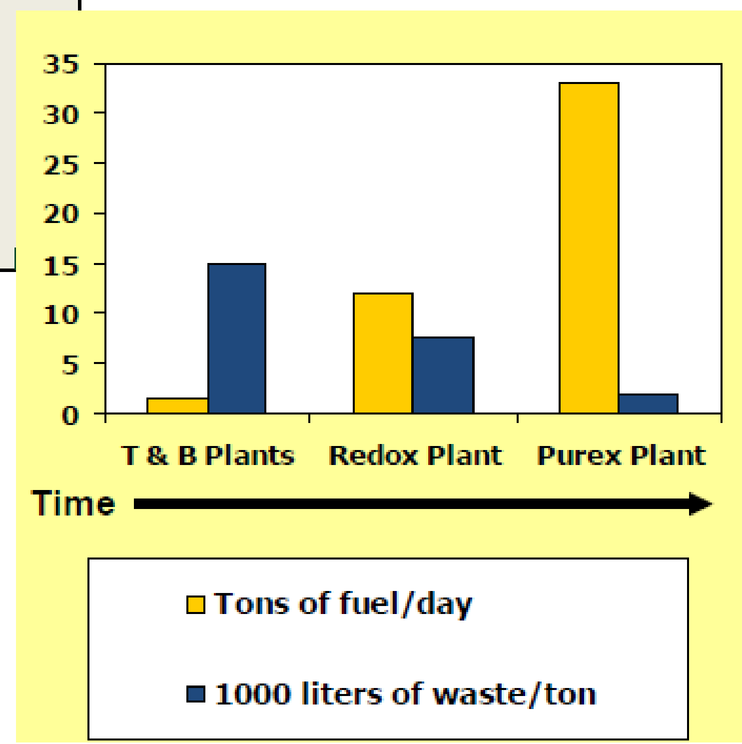
9 Reactors; 4 Fuel Reprocessing Flowsheets; 100,000 MT Fuel Processed

Chemical Processes and Resulting Waste

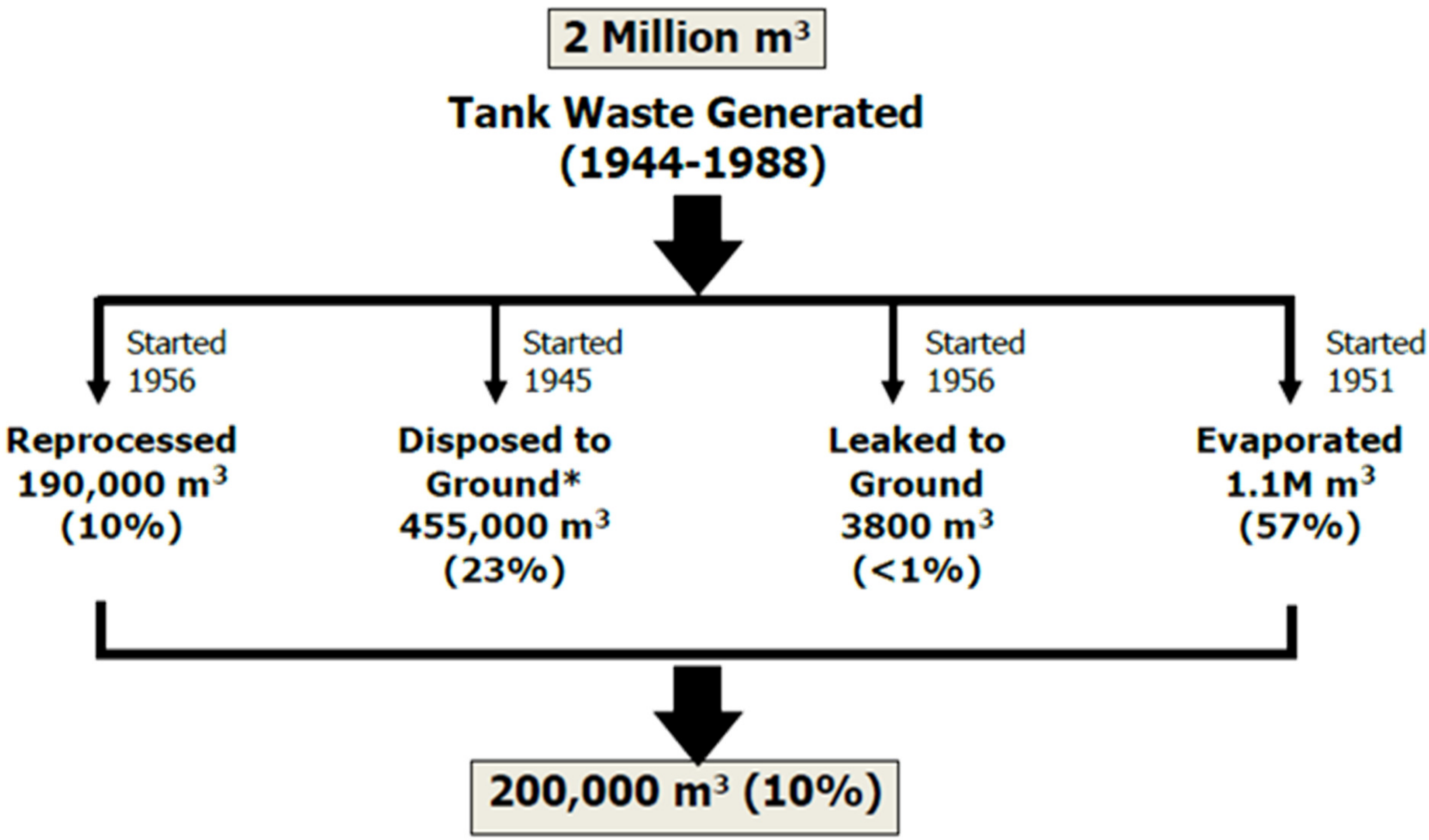
- Al Cladding Removal
  - rich in Na, **Al**, **Si**, OH
- Zr Cladding Removal
  - rich in **Zr**, **F**, Na
- Fuel Dissolution
  - rich in $\mathbf{NO_3}$
- $BiPO_4$ carrier ppt
  - rich in **Bi**, **P**, **Ca**, Mn, La, F, Fe, K, U, **S, Cr**
- REDOX SX
  - rich in **Al**, **Cr**, **S**, F, **Mn**, Fe
- PUREX SX
  - rich in **Fe**, **S**
- THOREX SX
  - rich in **Th**, P
- U Recovery
  - rich in **FeCN**, K, **Ni**, CO_3
- Cs/Sr Recovery
  - rich in P, Ca, S, organics
- Waste Neutralization/ Corrosion Control
  - rich in **Na**, **OH**, $\mathbf{NO_2}$, Cr
- Other
  - Atm. absorption ($\mathbf{CO_3}$, -OH)
  - Solvent washes (Na, K, Mn, CO_3)
  - Chemical impurities (**Cl**)
  - Radiolysis (NO_2)
  - Dash-5 (**Pu**, F)
  - Diatomaceous earth (Si)
  - Corrosion (Fe, **Ni**, Cr)

Hanford History

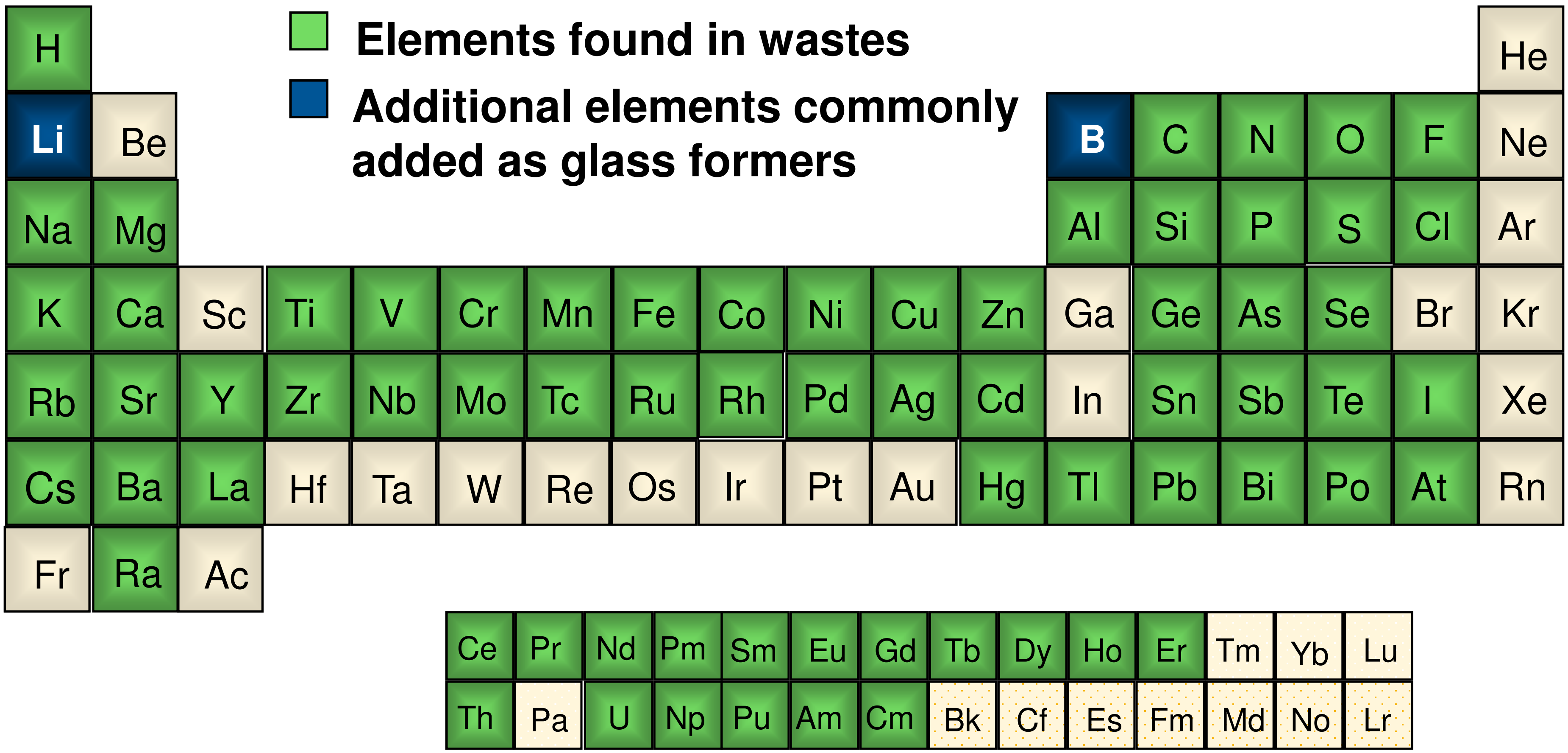




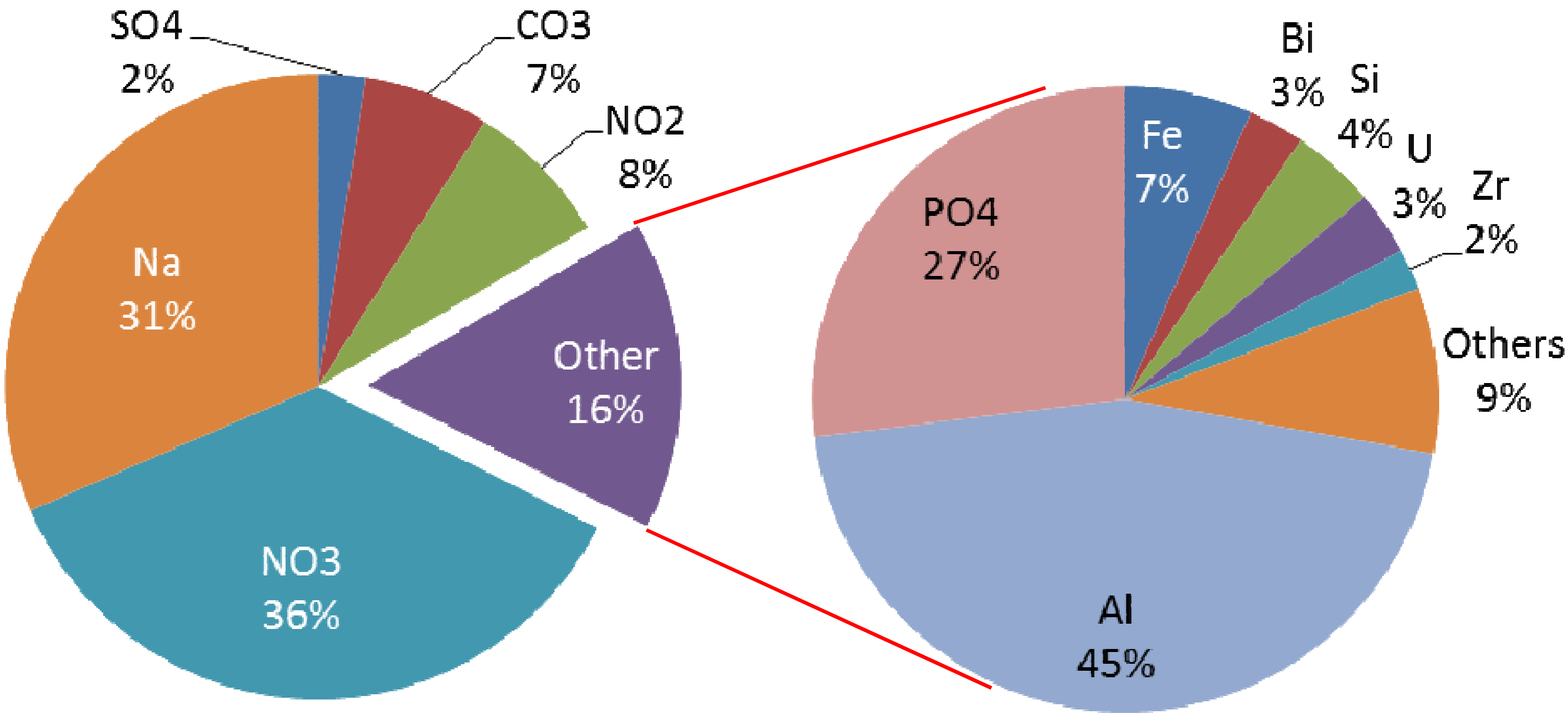
Hanford History, cont.



Overall Tank Composition



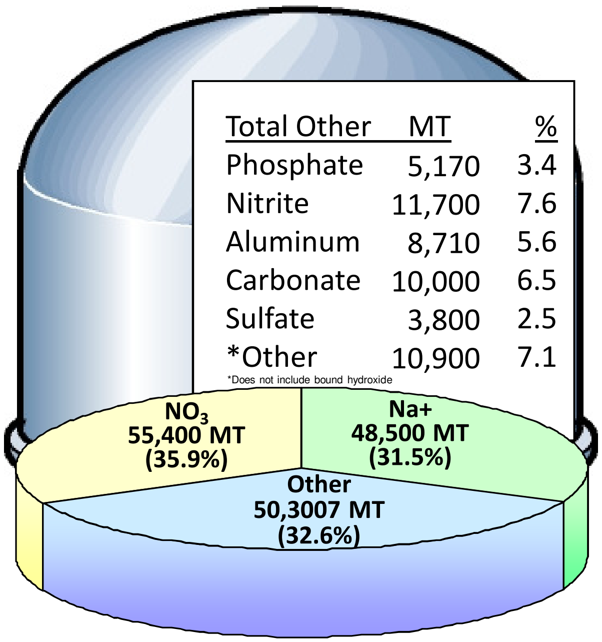
Hanford Tank Waste



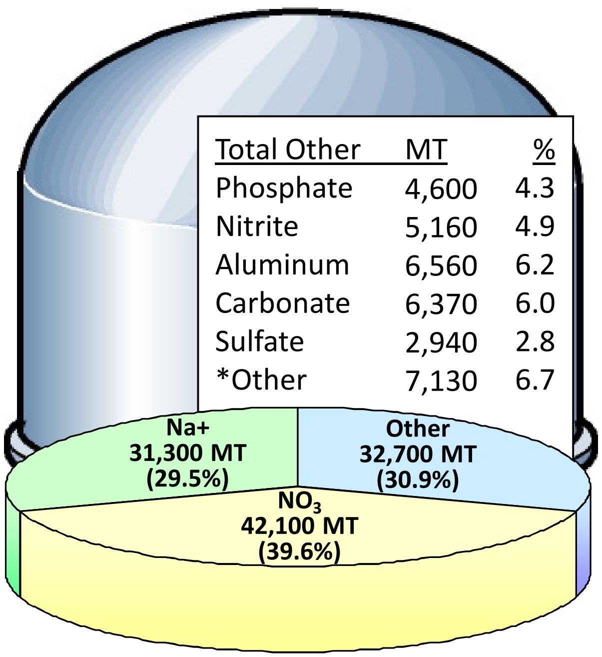
Best Basis Inventory, 2014

Chemical Inventory

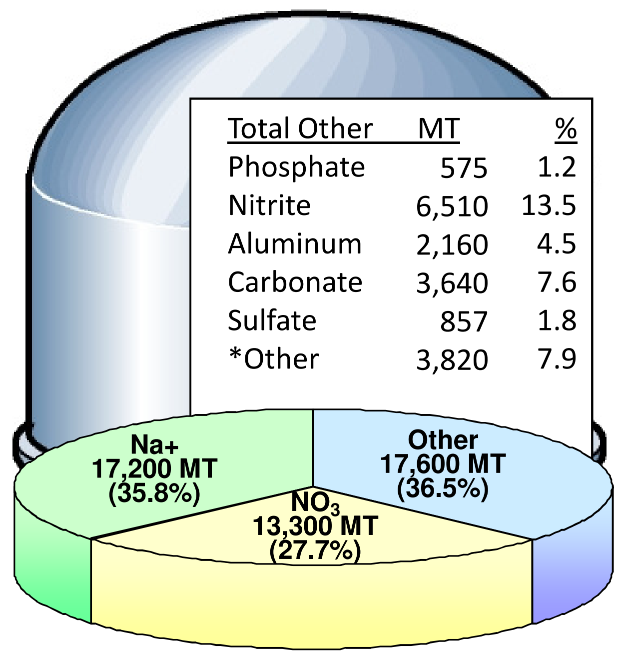
BBI, Jan. 2008



Total in All Tanks
154,000 Metric Tons



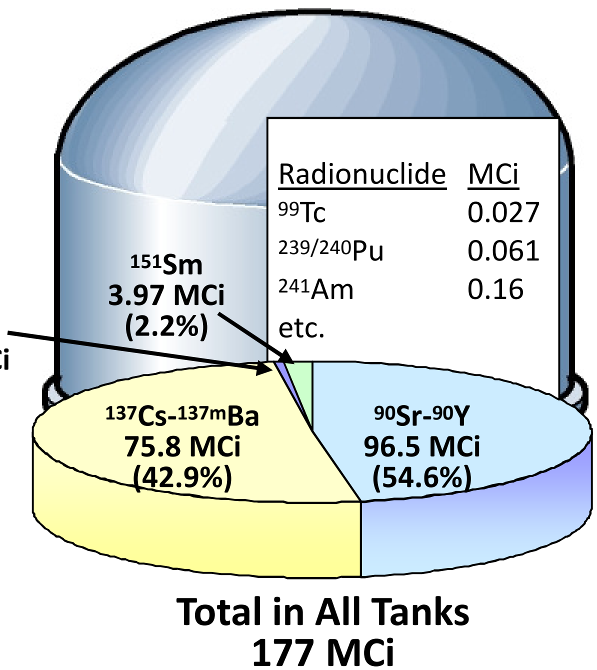
Single-Shell Tanks
106,000 Metric Tons

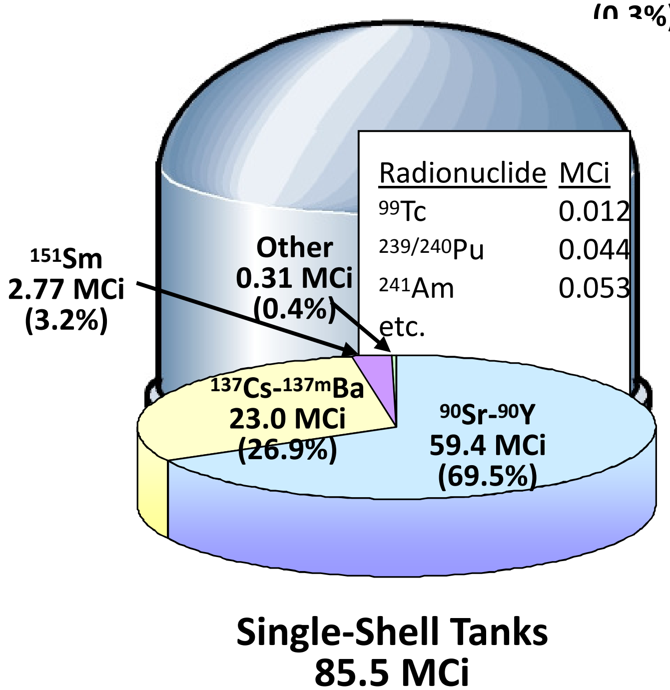


Double-Shell Tanks
48,100 Metric Tons

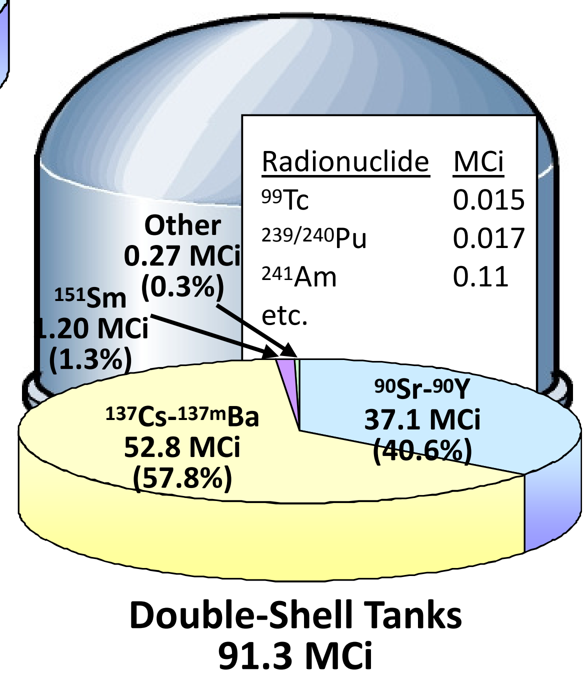
Herting and Barton 2008

Radionuclide Inventory





Decayed to January 1, 2008



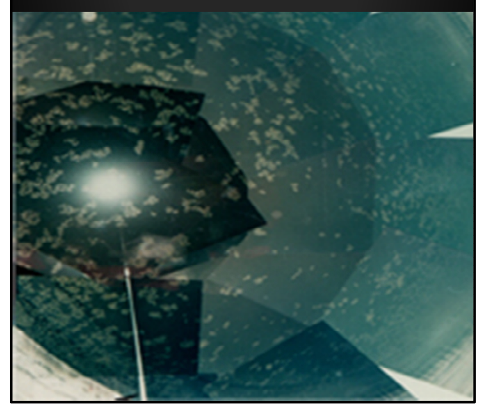
From: Herting and Barton 2008

Tank Waste Characterization/Feed Control to WTP

SALTCAKE
23 million gallons

SLUDGE
12 million gallons

SUPERNATE
21 million gallons



Saltcake

- Water-soluble
- White to black (usu. light brown)
- 10-50% H_2O
- High in Na, Al, anions, ^{137}Cs

Herting and Barton Tank Chemical and Radionuclide Inventories: Source, Occurrence, and Speciation, 2008

U-104

U-104

Sludge

- Wet mud
- Water-insoluble
- White to black (usu. dark brown)
- 50-80% H_2O
- High in Fe, Al, Si Mn, ^{90}Sr, TRU

Herting and Barton 2008

Tank T-111

Tank S-112

Tank SX-114 1987 (8701219-

Supernatant Liquid

- Pale yellow or green to coffee-colored
  (usually bright yellow)
- 50 – 90% H_2O
- Na^+ 10 M

  NO_3^- 3 M

  NO_2^- 2 M

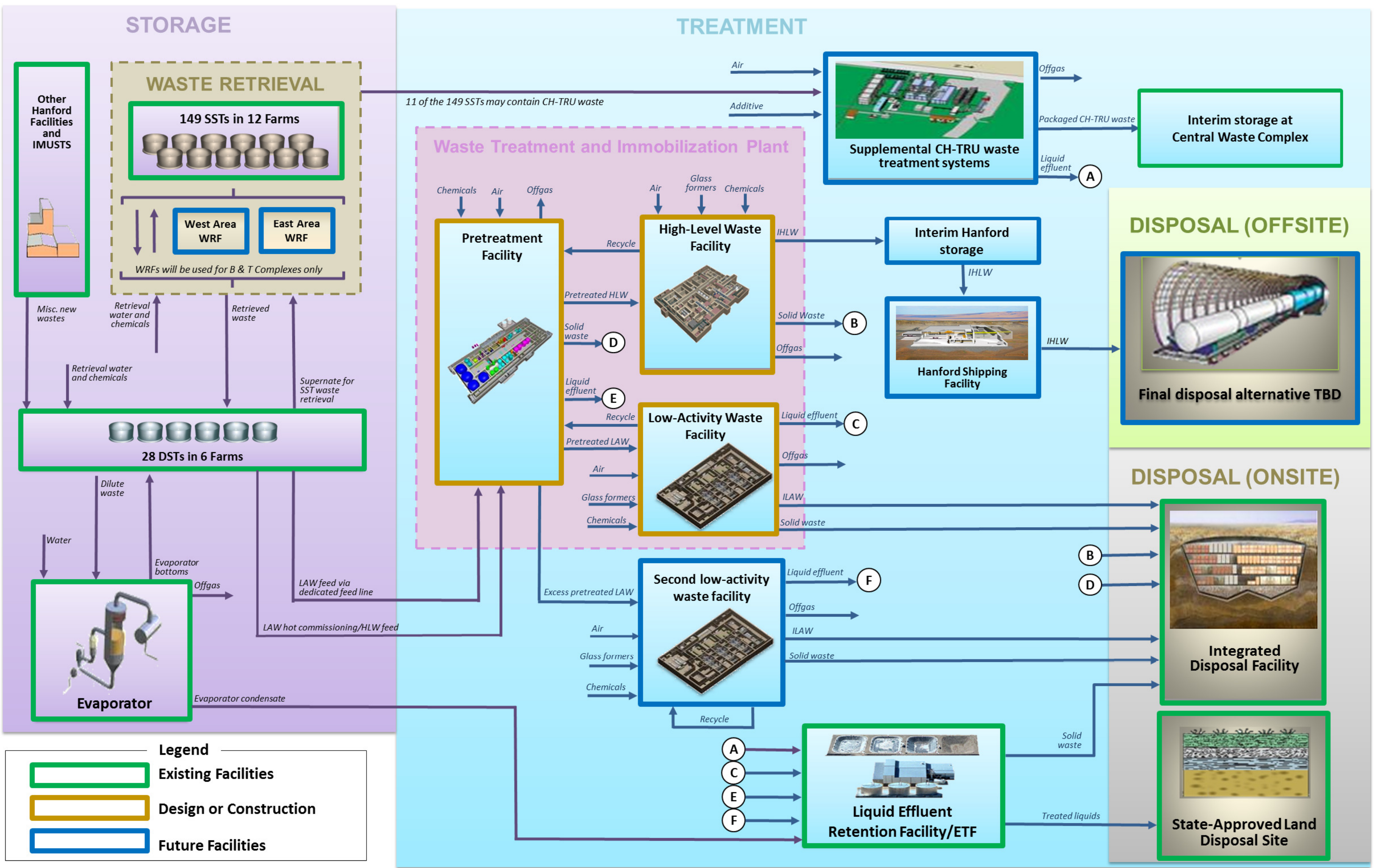
  OH^- 1 M

  $Al(OH)_4^-$ 0.5 M

  (all with wide variations)

Herting and Barton 2008

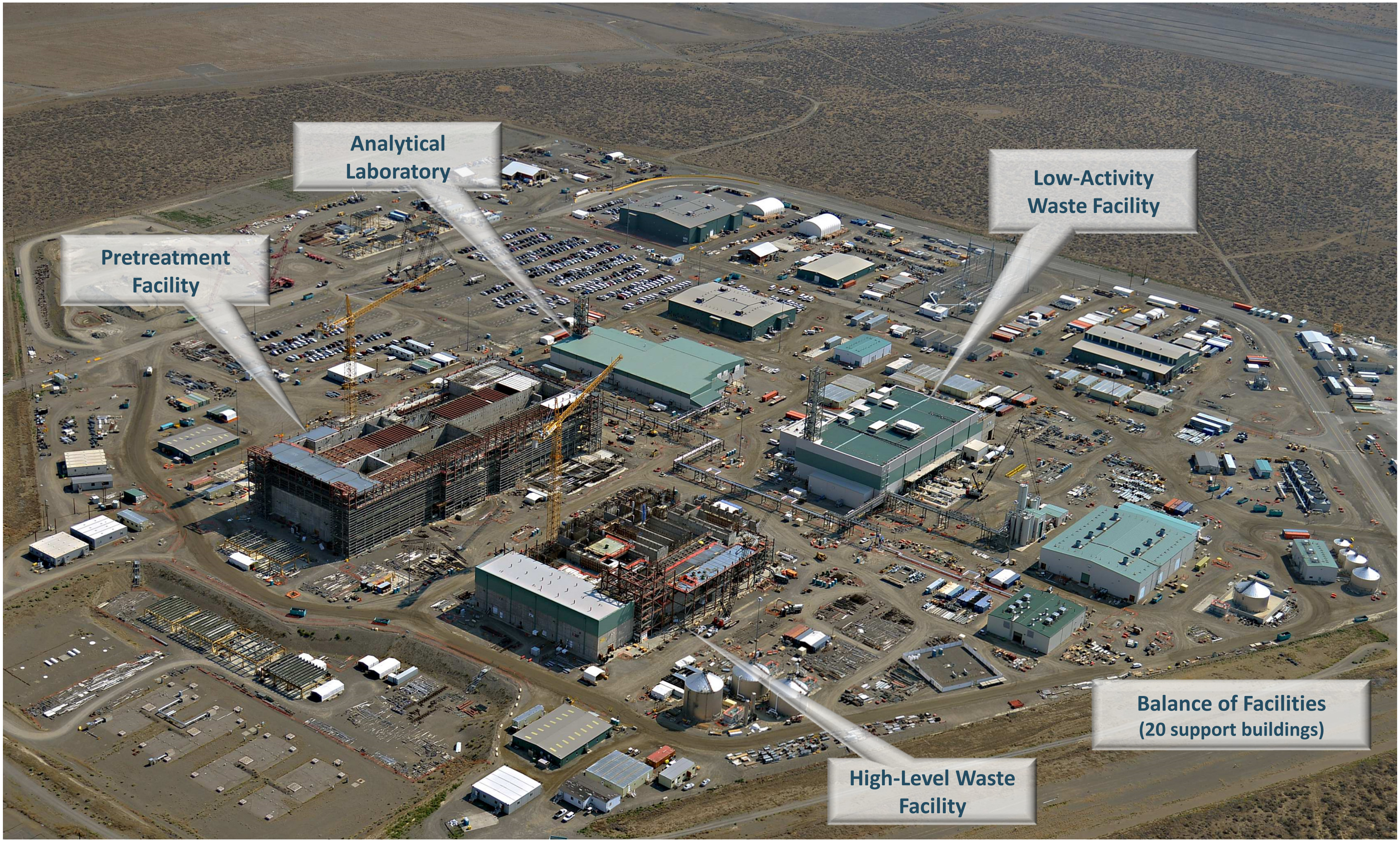
River Protection Project Flowsheet



What Happens in the WTP?

- Waste is received from PT (or LAWPS & EMF)
- Waste is sampled & analyzed for chemical/rad composition
- Waste is mixed with glass forming chemicals (GFCs) to target a compliant and processable glass
- Melter feed is fed to the melter, melted, and cast into cans to solidify into alkali-alumino-borosilicate glass waste form
- Canisters/containers are stored/cooled, sealed, decontaminated, and prepared for shipment out of the facility
- Off-gas is treated to meet release requirements
- Liquid and solid secondary wastes are managed and prepared for shipment out of the facility

Waste Treatment and Immobilization Plant



ORP Baseline Glass Formulation for HLW & LAW Treatment

- Current estimates (SP7: ORP-11242) project that ORP will produce 10,214 HLW canisters (30,845 MT glass). The *ca.* 79,056 MT of sodium (LAW processing basis) will produce 127,753 LAW containers (687,187 MT ILAW glass).
- The current glass formulation efforts have been conservative in terms of achievable waste loadings (WTP baseline).
- These formulations have been specified to ensure the glasses are homogenous, preclude secondary phases (sulfate-based salts or crystalline phases), are processable in joule-heated, ceramic-lined melters and meet WTP Contract terms.

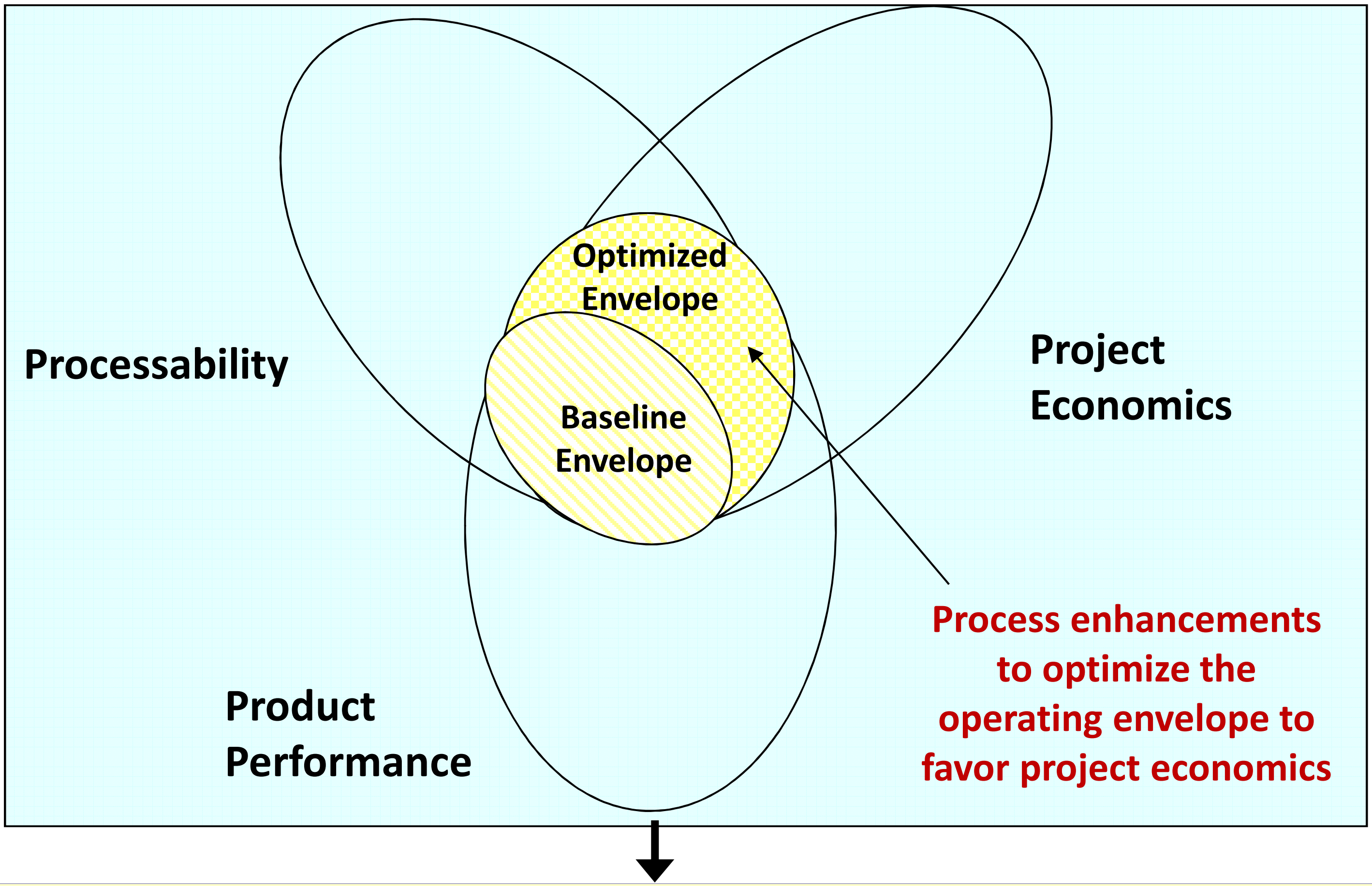
Formulating Glass

$$g_i = Ww_i + (1-W)a_i$$

$$P = \hat{P}_T\,(g_1, g_2, \ldots, gn)$$

For a given waste composition (w_i),
determine mineral addition (a_i),
to obtain glass composition (g_i),
with optimized properties (P),
and maximized waste loading (W)
The selection of properties to be optimized depends on melter technology and glass acceptability criteria

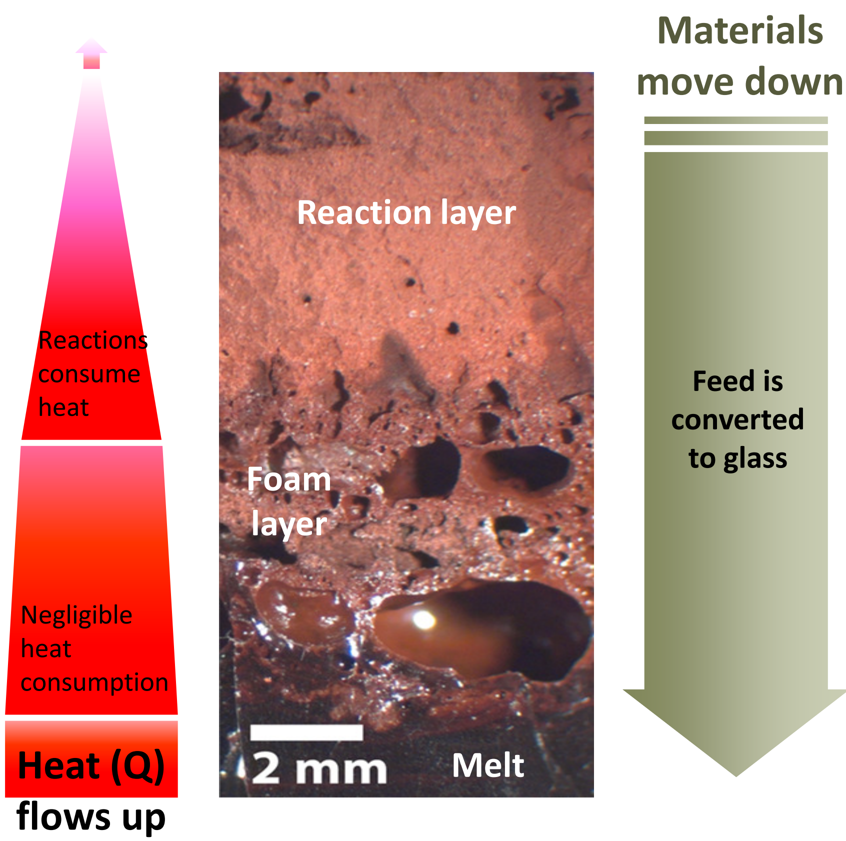
Process Optimization – HLW and LAW Vitrification Process Enhancements



Integration of glass formulation with melter engineering is crucial

Vitrification

Heat transfer



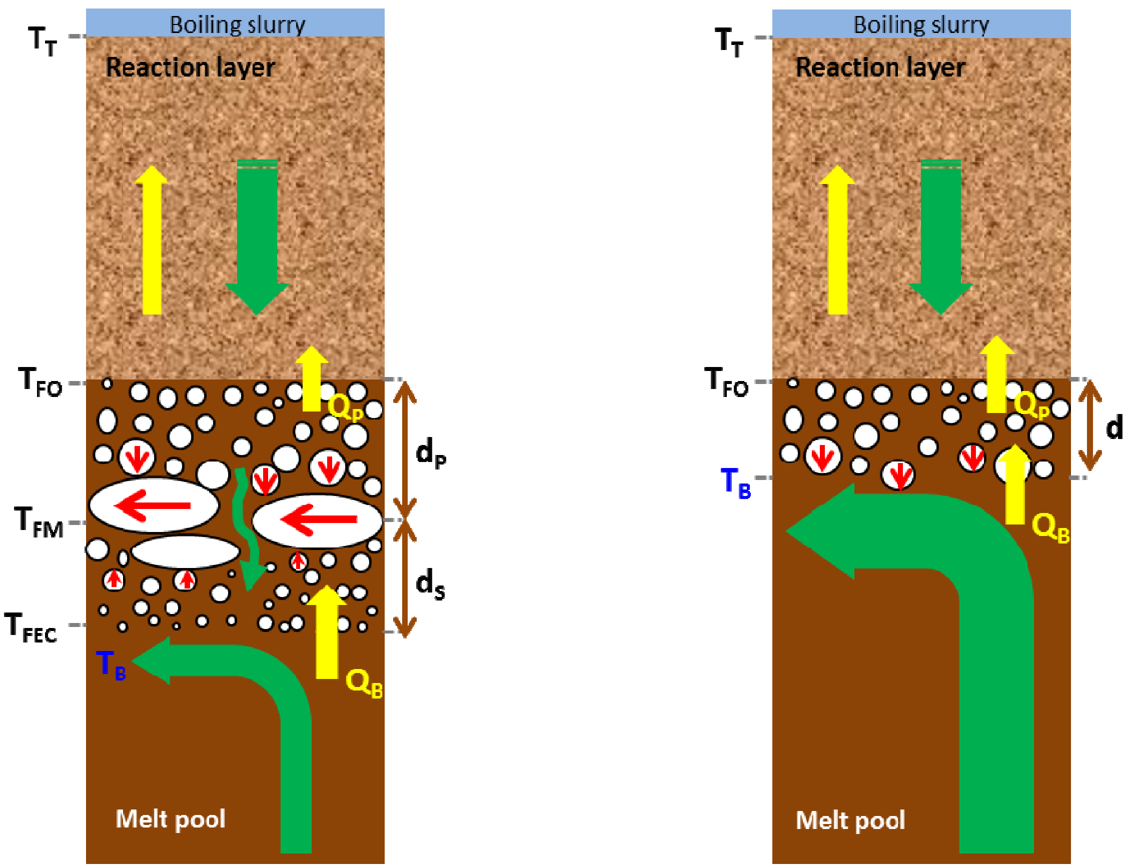
The feed-to-glass conversion heat is related to the rate of melting:

$$Q = (\Delta H + c_P \Delta T)j$$

Q is delivered through the cold-cap bottom and is transferred through the foam layer.

Q	conversion heat flux
ΔH	reaction heat
C_P	heat capacity
ΔT	cold cap temperature difference
j	melting rate

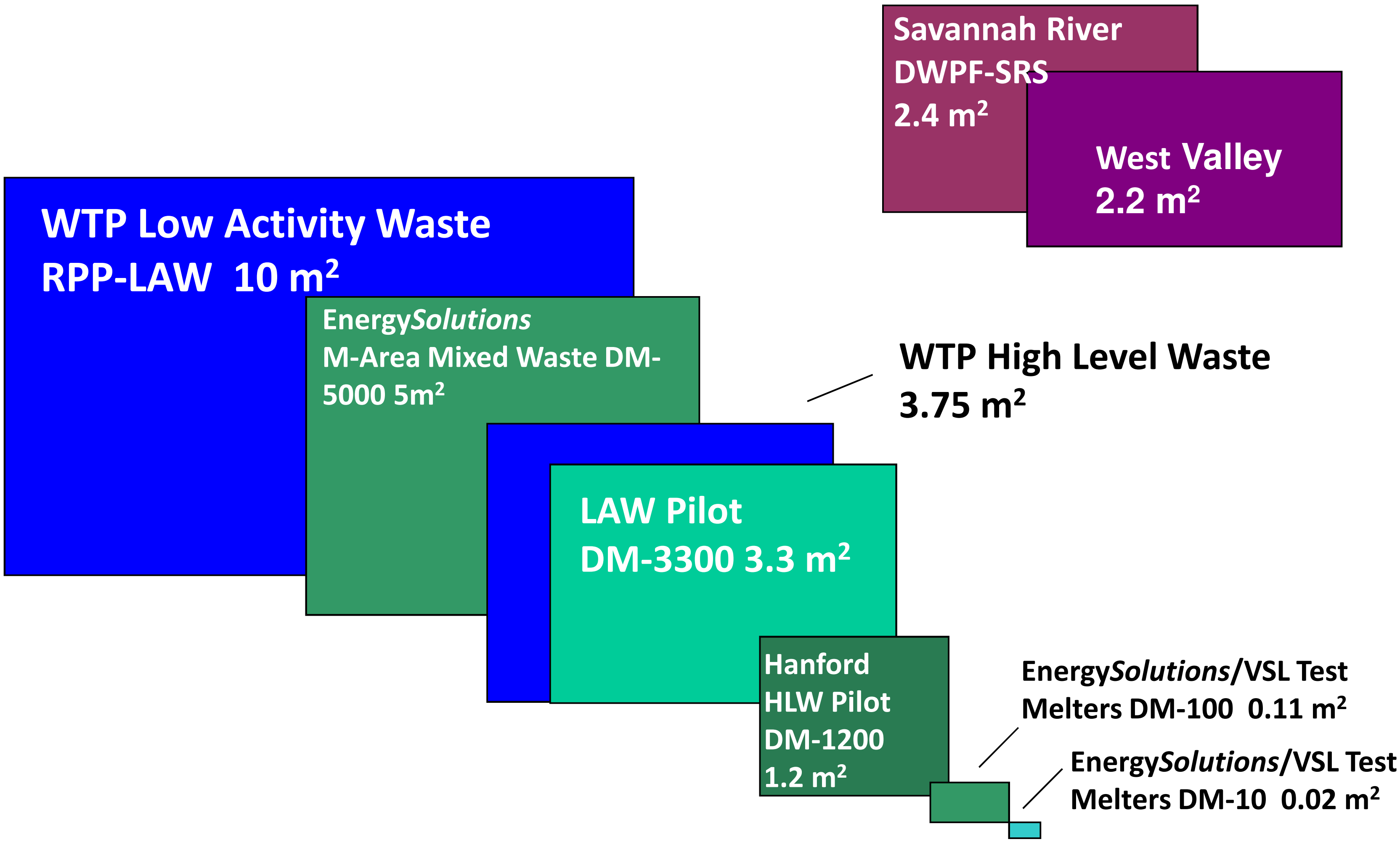
Enhanced heat flux by bubbling



(a) (b)

- Primary foam related to CO_2 gas goes down, grows, coalesces, and creates a cavity in the foam layer.
- Secondary foam related to O_2 gas goes up and accumulates under the cavity (or some foam maybe burst into the cavity) in the bottom of the cold cap.
- Gases in the cavity tends to move to the side of the cold cap and burst to atmosphere.

Melter Scale Comparison



LAW Vitrification

Selected Pellet Pictures

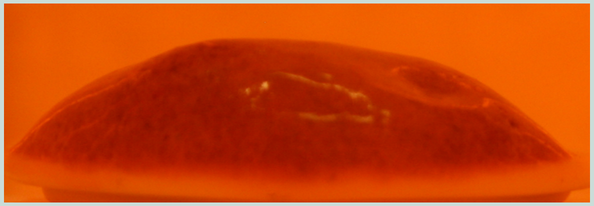
AN-102




625°C 675°C 725°C 775°C

AZ-102




AN-102

820°C 860°C

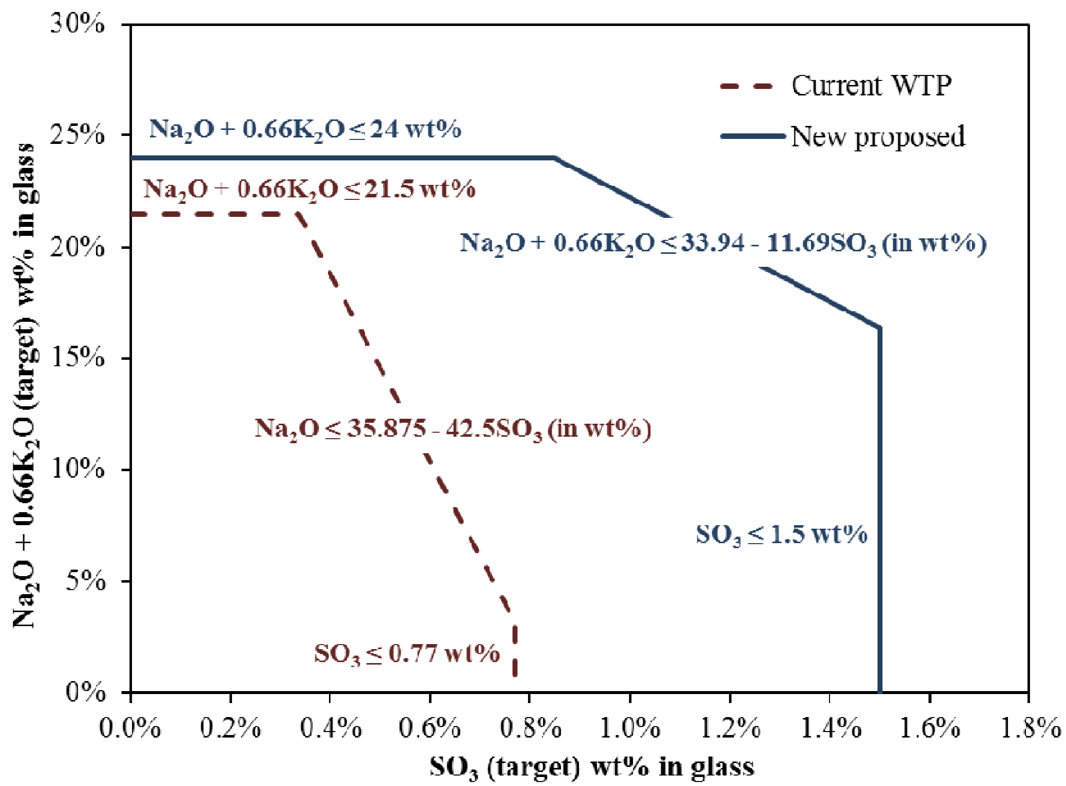

AZ-102

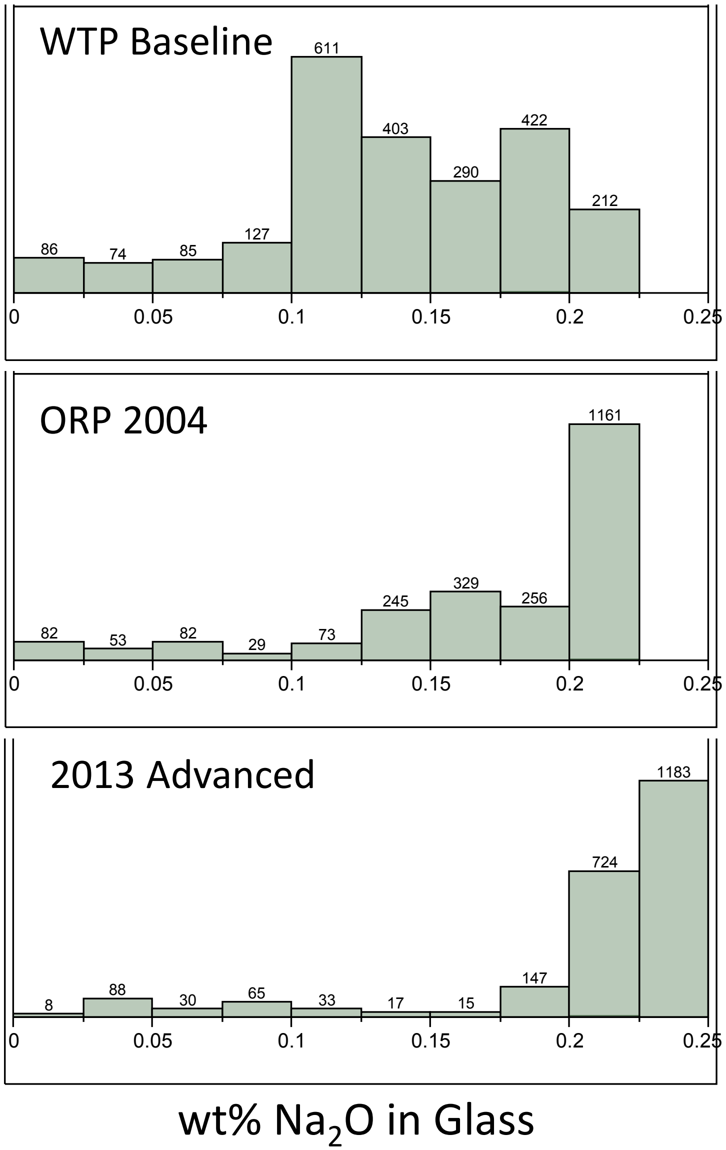
LAW Glass Property Constraints

- Processing
  - AB constraints on rad: Cs-137 < 0.3 Ci/m^3(glass)
  - Viscosity: 20 to 80 P at 1150°C
  - Electrical Conductivity: 0.1 to 0.7 S/cm at 1100 to 1200°C
  - No salt accumulation on melt surface
  - Acceptable corrosion of glass contact materials
  - Process rate: >30 MTG/d instantaneous, > 70% TOE
- Product Acceptance
  - Contract waste loading limit: waste Na_2O >14, 3, 10 wt%
  - Rad content: <Class C, <20 Ci/m^3 Sr-90, <3 Ci/m^3 Cs-137
  - Surface dose: < 500 mrem/h
  - Durability: < 2 g/m^2 PCT, <50 g/m^2/d VHT (predictable)
  - Phase stability: avoid phase changes or understand impacts on durability/regulatory compliance

Sulfur and Alkali Limits

- The factors limiting LAW glasses are:
  - chemical durability as measured by PCT and VHT for high Alk:SO_3 wastes
  - salt accumulation for low Alk:SO_3 wastes and high halide wastes





Composition Effects

Oxide	Al_2O_3	B_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	ZnO	ZrO_2	Other
Viscosity	↑	↓	↓	↔	↔	↓	↓	↓	↓	↑	↔	↑	
EC	↔	↔	↔	↔	↔	↑	↑	↔	↑	↓	↔	↔	
T_L, C_T (sp)	↑	↓	↓	↑	↑	↓	↓	↔	↓	↓	↑	↑	NiO, MnO↑
PCT	↓↑	↓↑	↔	↔	↔	↑	↑	↑	↑	↓	↔	↓	
VHT	↓↑	↓↔	↔	↔	↔	↑	↑	↔↑	↑	↓	↔	↓	
Nepheline	↑	↓	↑	↔	↔	↑	↑	↔	↑	↓	↔	↔	
Salt	↑	↓	↓	↑	↔	↓	↓	↔	↓	↑	↔	↔	SO_3, Cl ↑, V_2O_5↓
TCLP	↓	↑	↔	↔	↔	↑	↑	↔	↑	↓	↑	↓	MnO↑
Corrosion	↓	↔	↔	↓	↓	↑	↑	↔	↑	↓	↓	↓	NiO↓

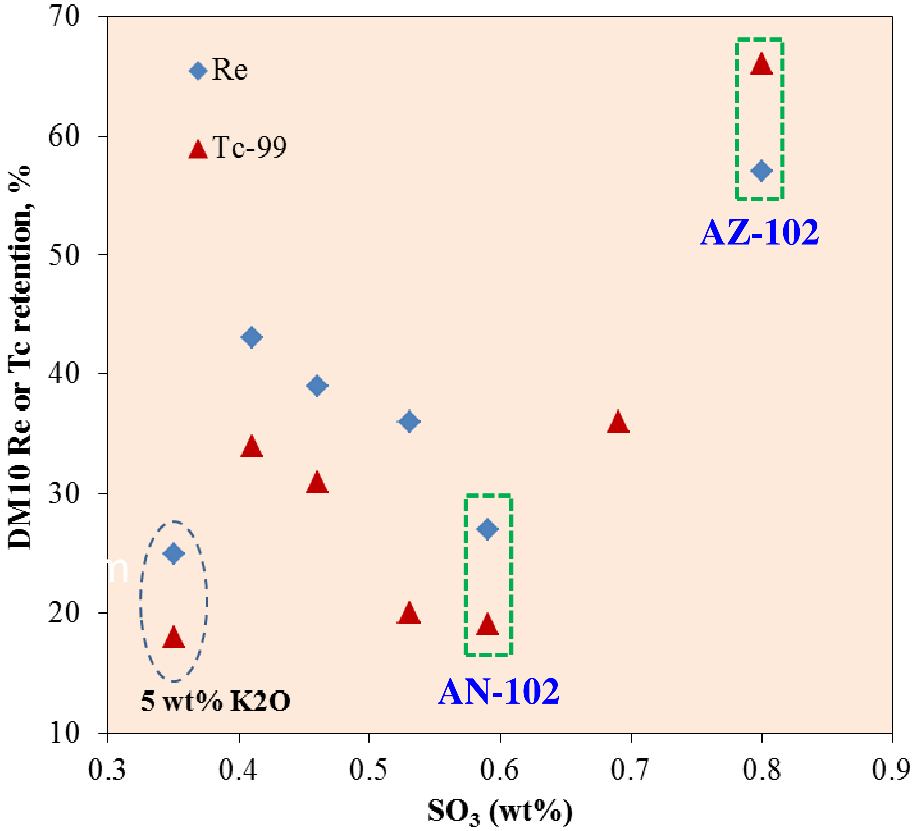
↑ - Increase property
↓ - Decrease property
↔ - Small effect on property
multiple arrows are for non-linear effects, first is for lower concentrations

'Significant' Waste Constituents

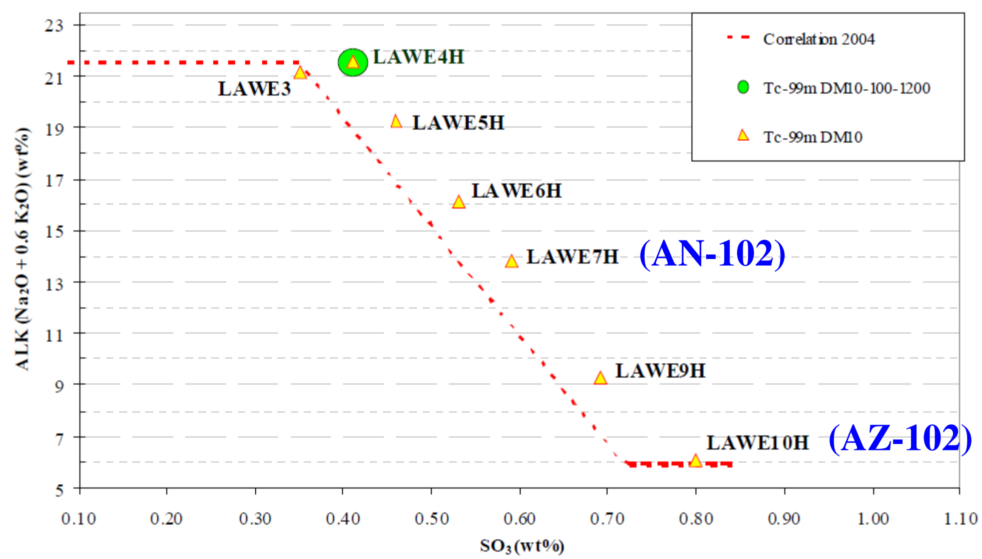
- Na, S, K: base waste loading/formulation
- NO_3, NO_2, TOC: reductant addition
- Cl, Cr, P: salt formation rules (impacts waste loading)
- Al: Alumina addition requirements
- Any other element with >0.5 wt% in glass: reporting
- Tc-99, I-129: IDF reporting
- Cs-137, Sr-90, class-C limits, TRU, total β/γ: AB, waste classification, reporting

Selection of Feeds

Based on Re and ^{99m}Tc Retention Data from small-scale melter (DM10) Tests by Vitreous State Laboratory (VSL)



"Na_2O + K_2O" wt% versus SO_3 wt% for 7 representative LAW feeds (WTP LAW glass formulation rules)

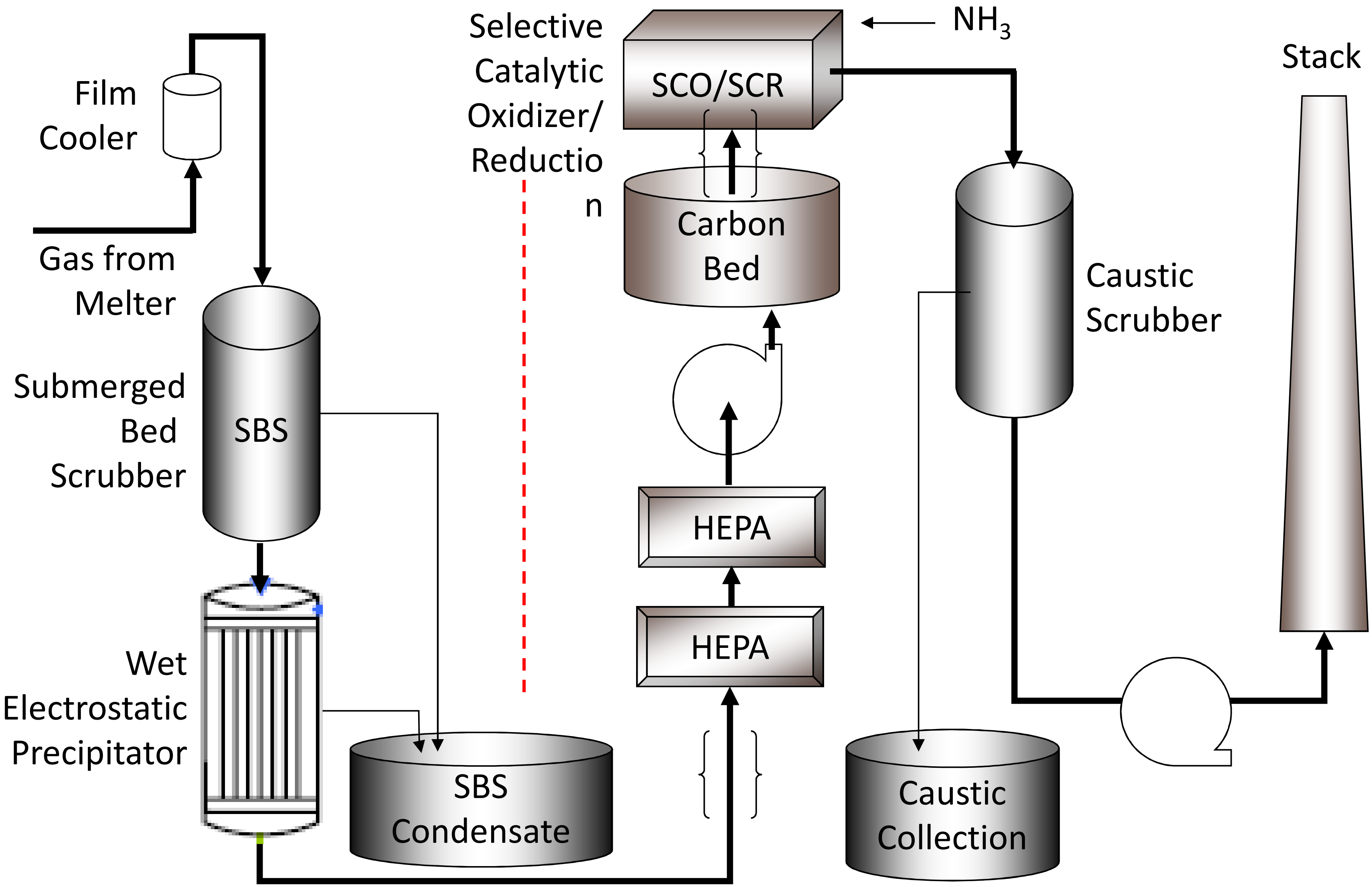


AN-102 and AZ-102 feeds with large difference in Re/Tc retention from DM10 tests were selected for initial set of crucible tests

- **AN-102: medium sulfur, high nitrates**
- **AZ-102: high sulfur, low nitrates**

Data and plot from VSL-11R2260-1, Rev 0

LAW Off-Gas Treatment



Kim and Vienna *Preliminary ILAW Formulation Algorithm Description*: 24590-LAW-RPT-RT-04-0003, Rev. 1, ORP-56321, 2012

HLW Vitrification

HLW Glass Property Constraints

- Processing
  - Viscosity: 20 to 80 P at 1150°C
  - Electrical Conductivity: 0.1 to 0.7 S/cm at 1100 to 1200°C
  - Acceptable crystal accumulation in the melter
  - No salt accumulation or phosphate scum on melt surface
  - Process rate: >7.5 MTG/d instantaneous, > 70% TOE
- Product Acceptance
  - Contract waste loading limit: Contract TS-1.1
  - Durability: PCT < DWPF EA glass (predictable)
  - Regulatory acceptability: CdO < 0.1 wt% or TCLP Cd < 0.48 mg/L and Tl_2O < 0.465 wt%
  - Phase stability: avoid phase changes or understand impacts on durability/regulatory compliance

Composition Effects

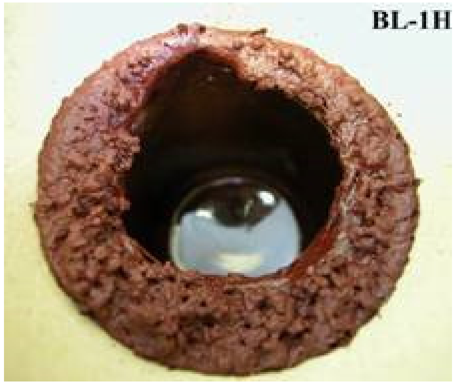
Oxide	Al_2O_3	B_2O_3	CaO	Cr_2O_3	Fe_2O_3	K_2O	Li_2O	MgO	Na_2O	SiO_2	ZnO	ZrO_2	Other
Viscosity	↑	↓	↓	↔	↔	↓	↓	↓	↓	↑	↔	↑	
EC	↔	↔	↔	↔	↔	↑	↑	↔	↑	↓	↔	↔	
T_L, C_T (sp)	↑	↓	↓	↑	↑	↓	↓	↔	↓	↓	↑	↑	NiO, MnO↑
PCT	↓↑	↓↑	↔	↔	↔	↑	↑	↑	↑	↓	↔	↓	
VHT	↓↑	↓↔	↔	↔	↔	↑	↑	↔↑	↑	↓	↔	↓	
Nepheline	↑	↓	↑	↔	↔	↑	↑	↔	↑	↓	↔	↔	
Salt	↑	↓	↓	↑	↔	↓	↓	↔	↓	↑	↔	↔	SO_3, Cl ↑, V_2O_5↓
TCLP	↓	↑	↔	↔	↔	↑	↑	↔	↑	↓	↑	↓	MnO↑
Corrosion	↓	↔	↔	↓	↓	↑	↑	↔	↑	↓	↓	↓	NiO↓

↑ - Increase property
↓ - Decrease property
↔ - Small effect on property
multiple arrows are for non-linear effects, first is for lower concentrations

Small-Scale Melt Rate Screening Results: ORP HLW Glasses with 24 wt% Al_2O_3

30 min

45 min



60 min

Initial Formulation

Reaction Time

30 min

60 min

Improved Formulation

Improvements confirmed in one-third scale pilot melter tests

VSL-08R1360-1, Rev.0; VSL-10R1690-1, Rev. 0

EGA and O_2 partial pressure by RAPIDOX

The melt is highly oversaturated with oxygen. Such a high oversaturation is not likely to arise solely from the iron redox equilibrium, but also from the oxygen “stored” in the feed from earlier batch decomposition reactions (mostly nitrates).

Foaming Curve & Secondary Foam

- **Detected CO_2 in the foam layer as a residual gas from the feed reaction and involved in the primary foam.**
- **Detected O_2 gas was from iron redox reaction and involved in the secondary foam.**
- **Influence of Gibbsite, Boehmite and Corundum**

Foaming in High Bi-P HLW Glass Melts

Results were used to modify glass formulations to mitigate melt foaming

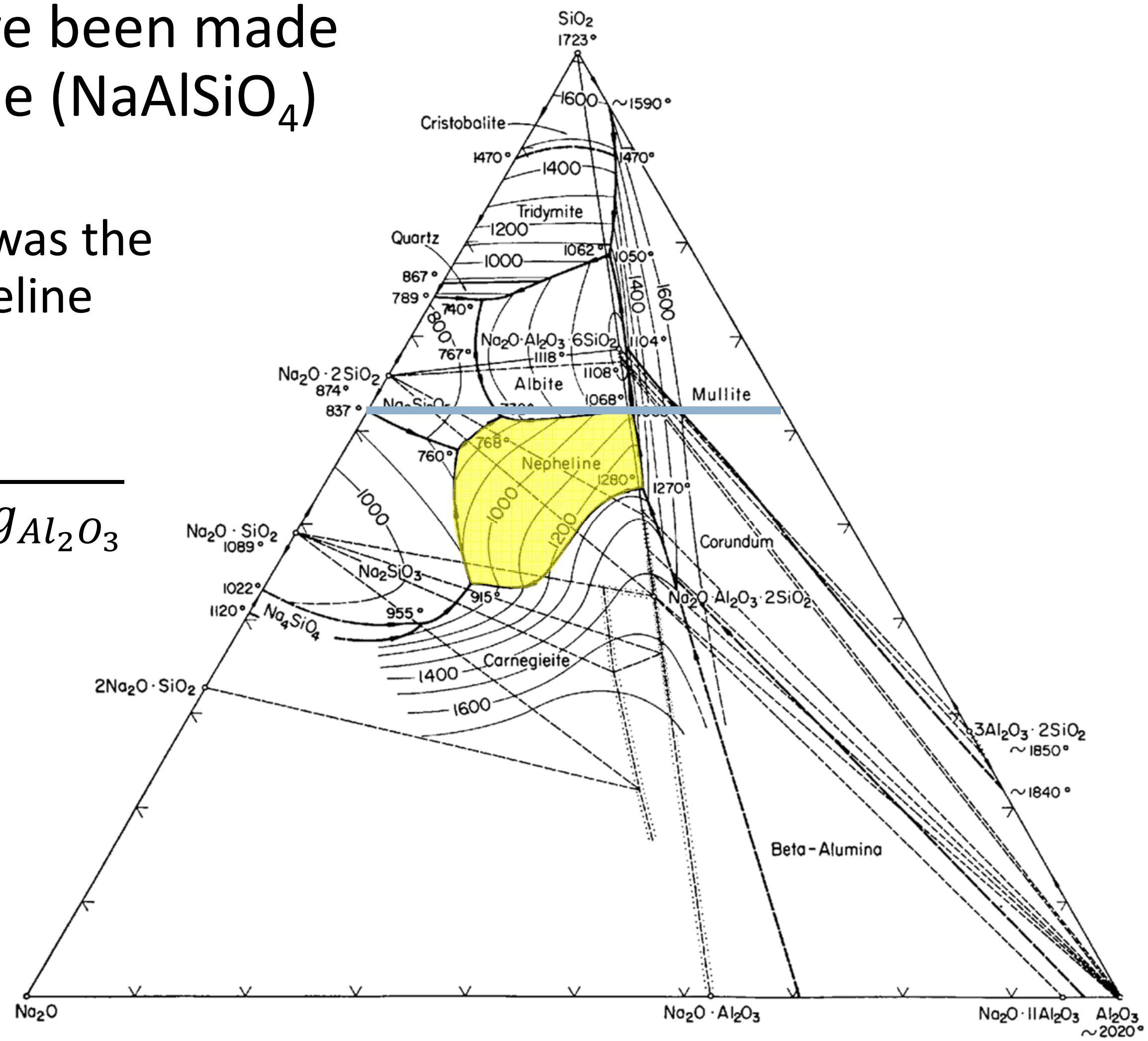
Melt Rate & Loading in High Fe Glasses

Improved formulations have been developed with both high melt rates and high waste loadings

Nepheline Precipitation

- Many attempts have been made to predict Nepheline ($NaAlSiO_4$) formation
  - the most successful was the Li et al. 1997[13] Nepheline discriminator:

$$ND = \frac{g_{SiO_2}}{g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}}$$



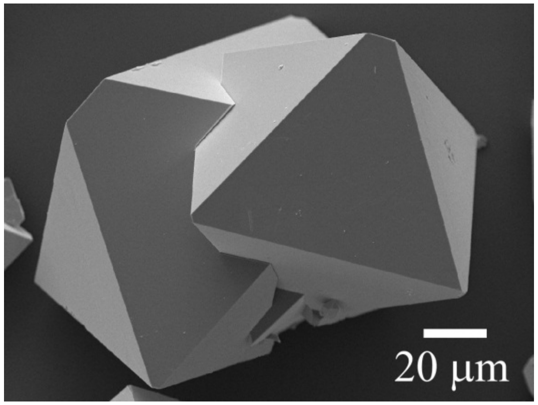
Sulfur Tolerance in HLW Glass

- **At concentrations above the sulfur tolerance limit, a sulfate containing salt accumulates on the melt surface**
- **About 22% of the projected HLW feed batches to the WTP are expected to be limited by sulfate (WTP Contract Minimum 0.5%)**

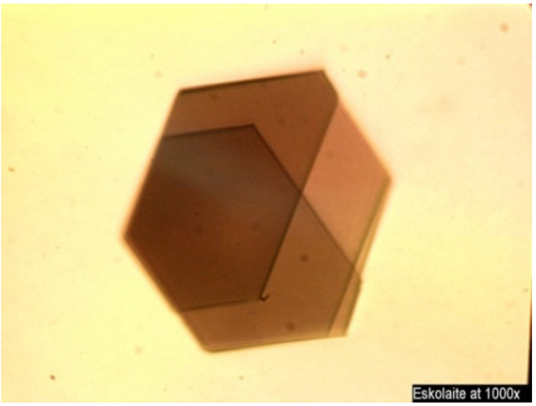
Crystal Tolerance

- **Two approaches considered**
  1. **Matyas et al. 2013 model for predicting the accumulation rate of spinel in the pour-spout riser at 850°C**
  2. **Limit the crystal fraction in the melt**

Spinel [Fe,Zn,Mn][Fe,Cr,Mn,Al]$_2$O$_4$



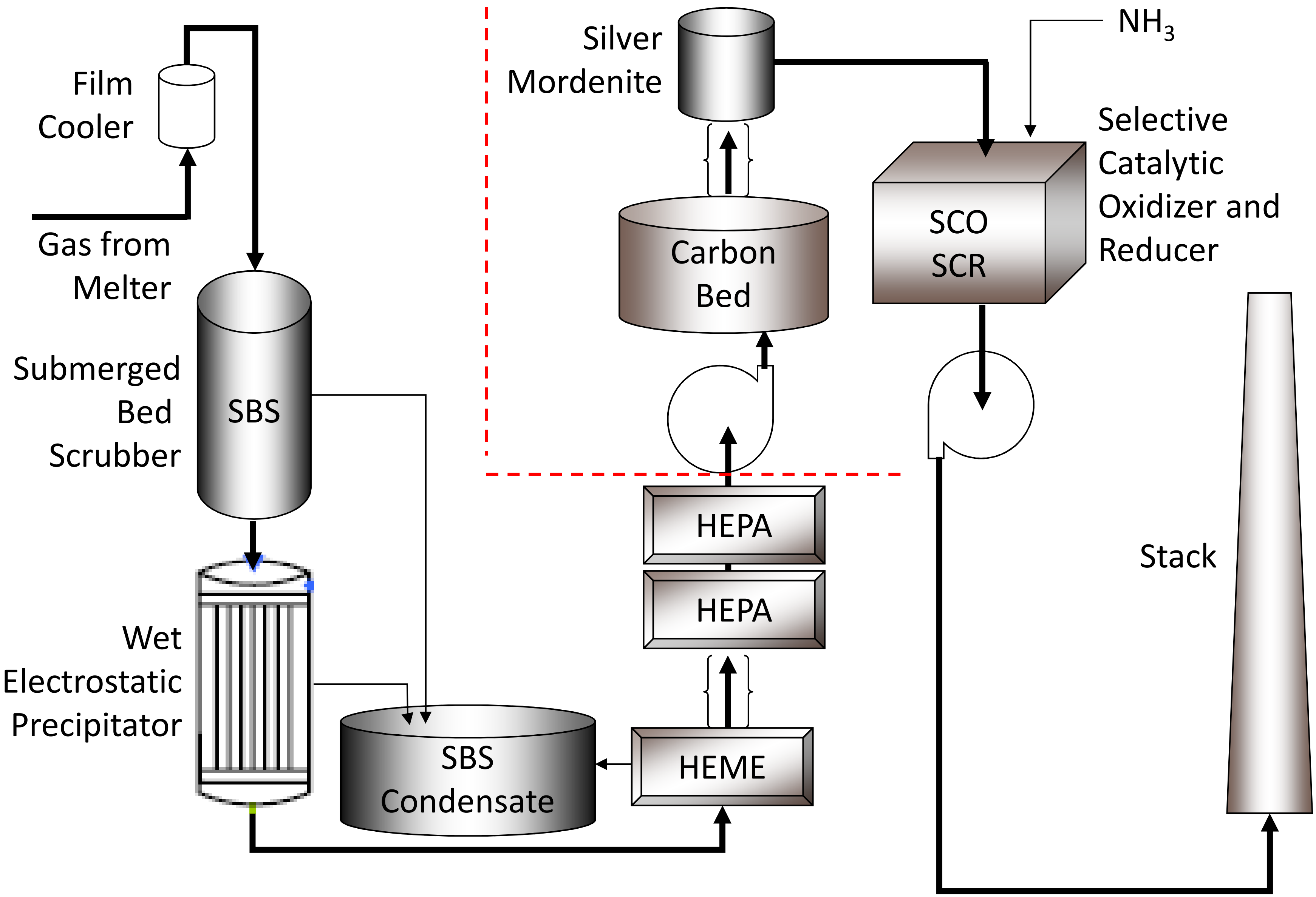
Eskolaite Cr_2O_3



'Significant' Waste Constituents

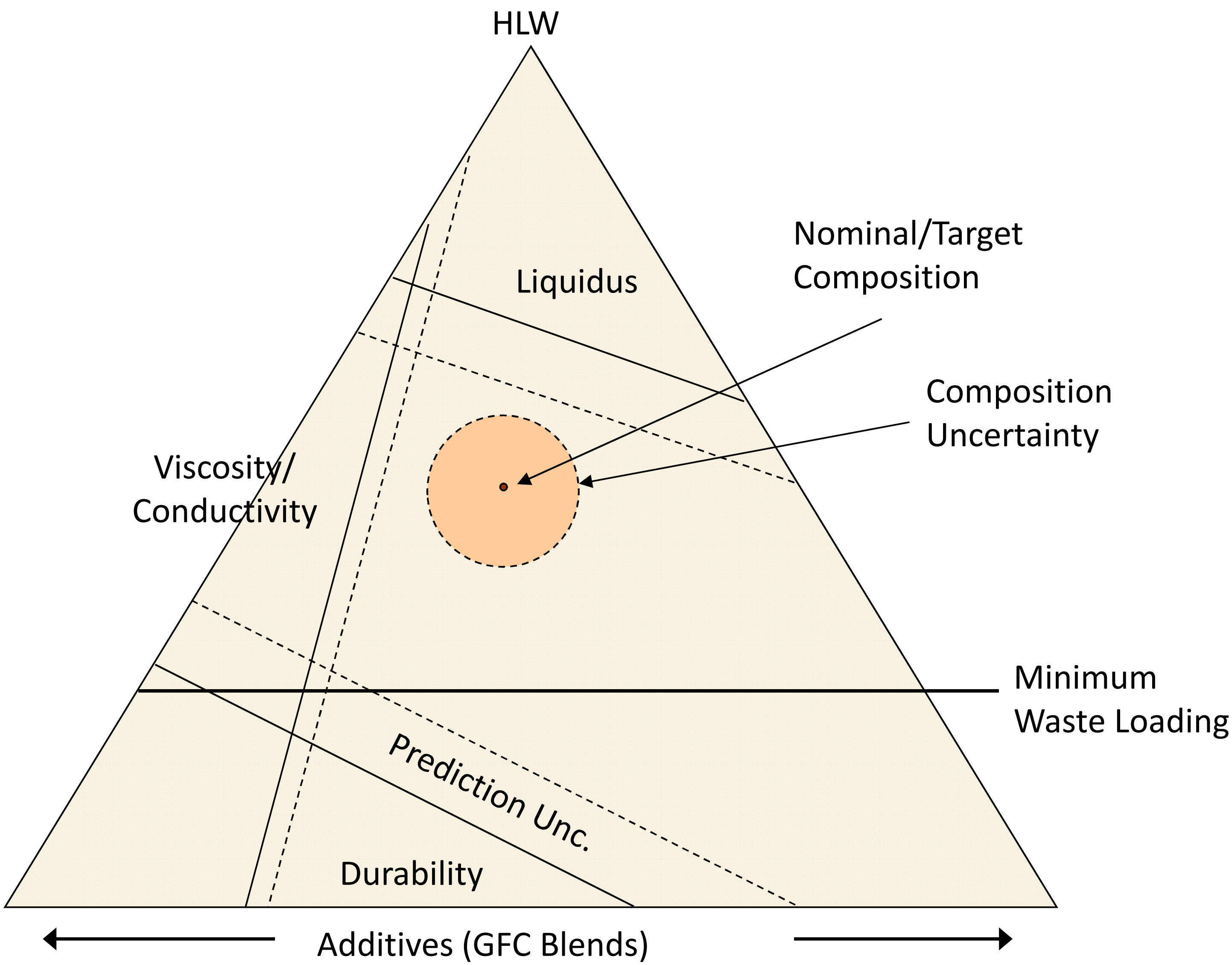
- Al, Ca, Cr, Fe, K, Mg, Mn, Na, Ni, P, S, Si, Th, U, Zr: base waste loading/formulation
- Any other element with >0.5 wt% in glass: comp. reporting
- NO_3, NO_2, TOC: reductant addition
- > 0.05% of the total radioactive inventory indexed to the years 2015 and 3115: rad. reporting

HLW Off-Gas Treatment

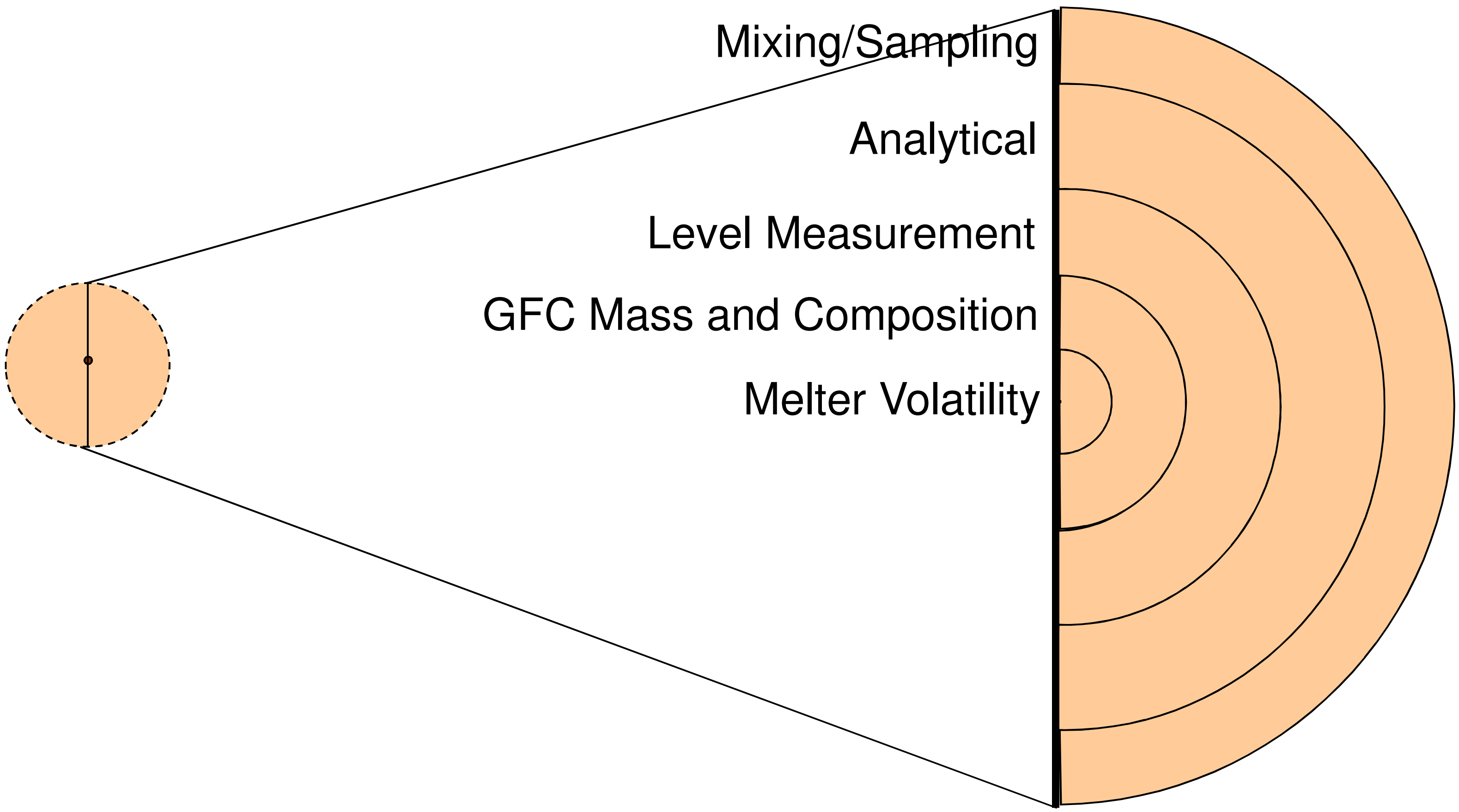


Vienna and Kim *Preliminary IHLW Formulation Algorithm Description*, 24590-HLW-RPT-RT-05-001, Rev. 1, 2014

Schematic of Processing Window



Composition Uncertainty



Enhanced Glass Models & the Impact on the Treatment Mission

Treatment Mission Projections

	BNI/WTP Baseline Models	2008 TUA* Baseline	2013 TUA Baseline	2013 TUA w/ caustic and oxidative leaching eliminated
HLW Canisters	18,400	14,838	8,223	13,534
LAW Containers	145,000	91,400	79,465	65,151
Total Canisters & Containers	163,000	106,238	87,688	78,685

* The “2008 models” were altered in anticipation of our work

24590-WTP-RPT-PE-13-003, Rev 0, 2013 Tank Utilization Assessment (TUA) Part 1: Potential Impact of Advanced Glass Models on the WTP, 3 December 2013

Lessons Learned and New Data, LAW

- Significantly new LAW PCT data available → fit new LAW PCT model
- Neural network VHT model was very difficult to implement and not sufficiently predictive of new data → find different form of models that are easier to apply and more predictive
- LAW Viscosity model was not refit in 2013 but significant new data available since 2007 → fit new LAW viscosity model
- 29 new melter test data with LAW sulfate solubility validated this model well → no change in LAW sulfate model
- Need for refractory corrosion constraint with high loaded LAW glasses → VSL recently published preliminary K3 corrosion model
- Halide rules split between conservative and optimistic approach added confusion and new data added, suggesting the need for a new approach → new halide/chromium rules added based on optimization

Lessons Learned and New Data, HLW

- The spinel c_T under-predicts new data at the higher spinel fraction → refit model without combined c and T (e.g., c_{950} or $T_{2\%}$)
- Neural network nepheline model was very difficult to implement and not sufficiently predictive of new data → find different form of models that are easier to apply and more predictive
- New HLW sulfate solubility data (13 glasses) showed the combined LAW + HLW model significantly under-predicted new data → fit separate HLW sulfate solubility model
- New HLW PCT data showed that the previous PCT model was not sufficiently predictive of PCT responses for glasses with Al_2O_3 concentrations > 25 wt% → fit new HLW PCT model trying new methods of accounting for non-linear effects of Al_2O_3
- HLW Viscosity model was not refit in 2013 but significant new data available since 2009 → fit new HLW viscosity model

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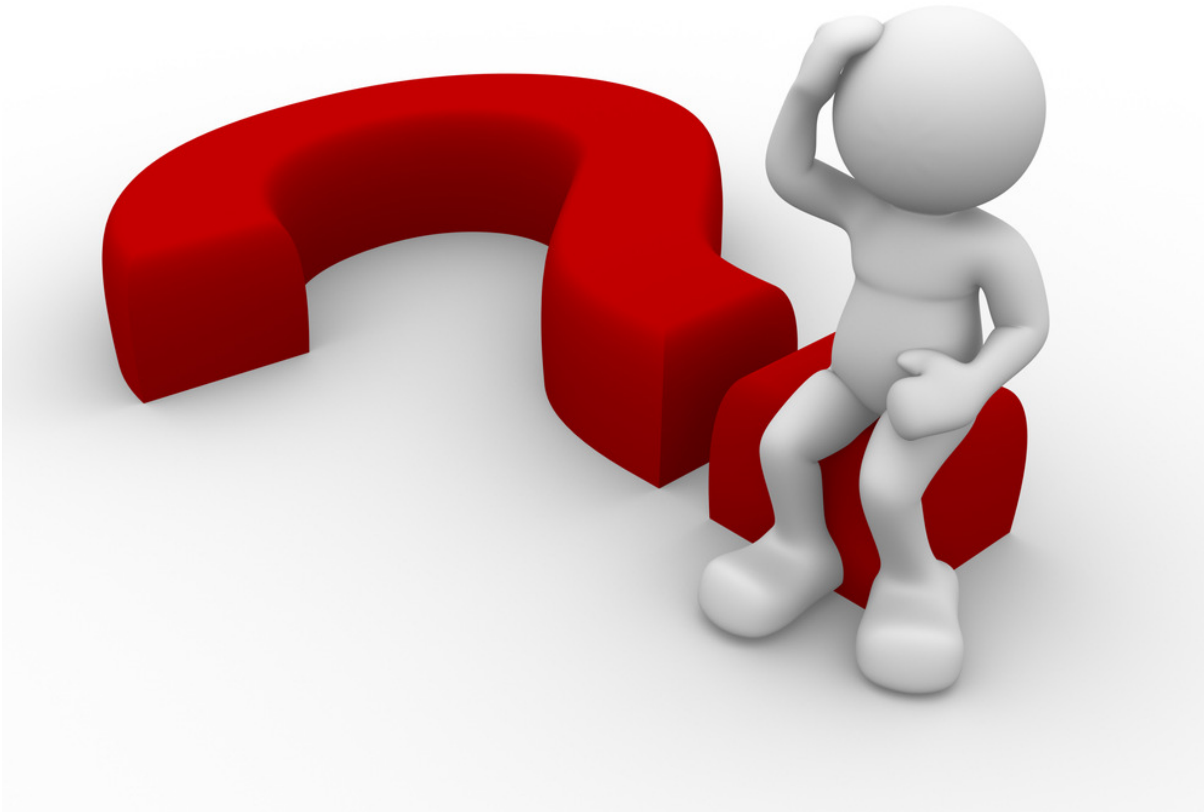

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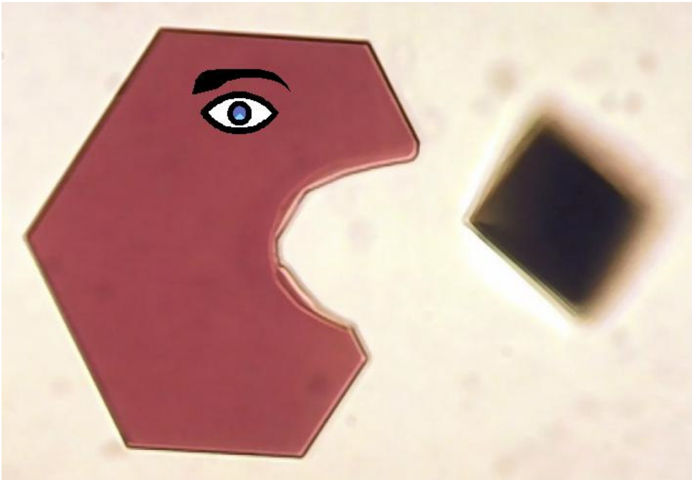


Oxide Compositions of Limiting HLW Streams (wt%)

Waste Component	Bi Limited	Cr Limited	Al Limited	Al and Na Limited
Al_2O_3	22.45%	25.53%	49.21%	43.30%
B_2O_3	0.58%	0.53%	0.39%	0.74%
CaO	1.61%	2.47%	2.21%	1.47%
Fe_2O_3	13.40%	13.13%	12.11%	5.71%
Li_2O	0.31%	0.36%	0.35%	0.15%
MgO	0.82%	0.16%	0.24%	0.44%
Na_2O	12.97%	20.09%	7.35%	25.79%
SiO_2	12.04%	10.56%	10.05%	6.22%
TiO_2	0.30%	0.01%	0.02%	0.35%
ZnO	0.31%	0.25%	0.17%	0.36%
ZrO_2	0.40%	0.11%	0.81%	0.25%
SO_3	0.91%	1.52%	0.41%	0.44%
Bi_2O_3	12.91%	7.29%	2.35%	2.35%
ThO_2	0.25%	0.04%	0.37%	0.04%
Cr_2O_3	1.00%	3.07%	1.07%	1.44%
K_2O	0.89%	0.37%	0.29%	1.34%
U_3O_8	3.48%	7.59%	7.25%	4.58%
BaO	0.02%	0.03%	0.11%	0.06%
CdO	0.00%	0.01%	0.05%	0.02%
NiO	3.71%	1.06%	0.82%	0.20%
PbO	0.48%	0.48%	0.84%	0.18%
P_2O_5	9.60%	3.34%	2.16%	4.10%
F-	1.58%	2.00%	1.37%	0.46%
Total	100.00%	100.00%	100.00%	100.00%

Table TS-8.3 High-Level Waste Feed Unwashed Solids Maximum Radionuclide Composition (Curies per 100 grams non-volatile waste oxides)

Isotope	Maximum (Ci / 100 grams waste oxides)	Isotope	Maximum (Ci / 100 grams waste oxides)	Isotope	Maximum (Ci / 100 grams waste oxides)
^{3}H	6.5E-05	^{129}I	2.9E-07	^{237}Np	7.4E-05
^{14}C	6.5E-06	^{137}Cs	1.5E00	^{238}Pu	3.5E-04
^{60}Co	1E-02	^{152}Eu	4.8E-04	^{239}Pu	3.1E-03
^{90}Sr	1E+01	^{154}Eu	5.2E-02	^{241}Pu	2.2E-02
^{99}Tc	1.5E-02			^{241}Am	9.0E-02
^{125}Sb	3.2E-02	^{233}U	4.5E-06 (all tanks except AY-101/C-104)(2.0E-04 for AY-101/C-104 only)	$^{243+244}Cm$	3.0E-03
^{126}Sn	1.5E-04	^{235}U	2.5E-07		

Table TS-7.1 Low-Activity Waste Chemical Composition, Soluble Fraction Only

	Maximum Ratio, analyte (mole) to sodium (mole)		
Chemical Analyte	**Envelope A**	**Envelope B**	**Envelope C[3]**
Al	**2.5E-01**	**2.5E-01**	**2.5E-01**
Ba	**1.0E-04**	**1.0E-04**	**1.0E-04**
Ca	**4.0E-02**	**4.0E-02**	**4.0E-02**
Cd	**4.0E-03**	**4.0E-03**	**4.0E-03**
Cl	**3.7E-02**	**8.9E-02**	**3.7E-02**
Cr	**6.9E-03**	**2.0E-02**	**6.9E-03**
F	**9.1E-02**	**2.0E-01**	**9.1E-02**
Fe	**1.0E-02**	**1.0E-02**	**1.0E-02**
Hg	**1.4E-05**	**1.4E-05**	**1.4E-05**
K	**1.8E-01**	**1.8E-01**	**1.8E-01**
La	**8.3E-05**	**8.3E-05**	**8.3E-05**
Ni	**3.0E-03**	**3.0E-03**	**3.0E-03**
NO_2	**3.8E-01**	**3.8E-01**	**3.8E-01**
NO_3	**8.0E-01**	**8.0E-01**	**8.0E-01**
Pb	**6.8E-04**	**6.8E-04**	**6.8E-04**
PO_4	**3.8E-02**	**1.3E-01**	**3.8E-02**
SO_4	**1.0E-02**	**7.0E-02**	**2.0E-02**
TIC[1]	**3.0E-01**	**3.0E-01**	**3.0E-01**
TOC[2]	**5.0E-01**	**5.0E-01**	**5.0E-01**
U	**1.2E-03**	**1.2E-03**	**1.2E-03**

Notes:
1. Mole of inorganic carbon atoms/mole sodium.
2. Mole of organic carbon atoms/mole sodium.
3. Envelope C LAW is limited to complexed tank wastes from Hanford tanks AN-102 and AN-107.

Table TS-7.2 Low-Activity Waste Radionuclide Content, Soluble Fraction Only Maximum Ratio, radionuclide to sodium (mole)

Radionuclide	Envelope A		Envelope B		Envelope C	
	Bq	uCi	Bq	uCi	Bq	uCi
TRU	4.80E+05	1.30E+01	4.80E+05	1.30E+01	3.00E+06	8.11E+01
^{137}Cs	4.30E+09	1.16E+05	2.00E+10	5.41E+05	4.30E+09	1.16E+05
^{90}SR	4.40E+07	1.19E+03	4.40E+07	1.19E+03	8.00E+08	2.16E+04
^{99}Tc	7.10E+06	1.92E+02	7.10E+06	1.92E+02	7.10E+06	1.92E+02
^{60}Co	6.10E+04	1.65E+00	6.10E+04	1.65E+00	3.70E+05	1.00E+01
^{154}Eu	6.00E+05	1.62E+01	6.00E+05	1.62E+01	4.30E+06	1.16E+02

Notes:

1. The activity limit shall apply to the feed certification date.
2. TRU is defined as: Alpha-emitting radionuclides with an atomic number greater than 92 with half-life greater than 20 years.

Some radionuclides, such as ^{90}Sr and ^{137}Cs, have daughters with relatively short half-lives. These daughters have not been listed in this table. However, they are present in concentrations associated with the normal decay chains of the radionuclides.

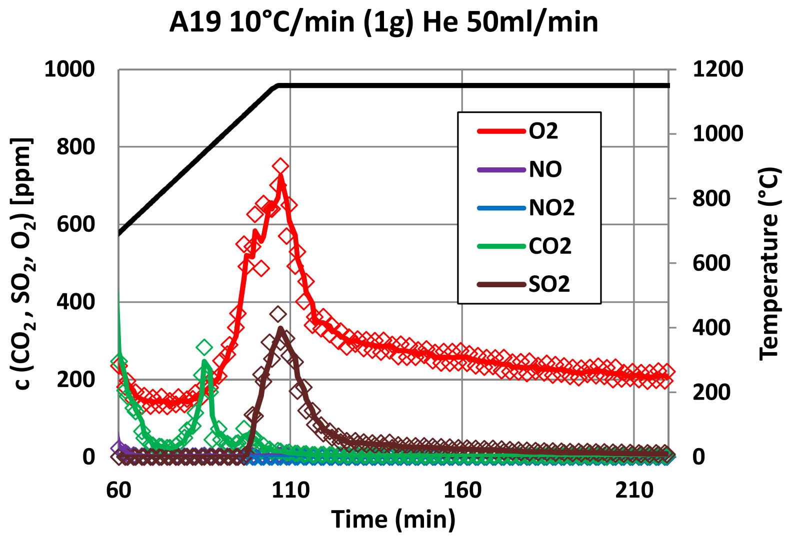
1Bq = 2.703 e-5 uCi

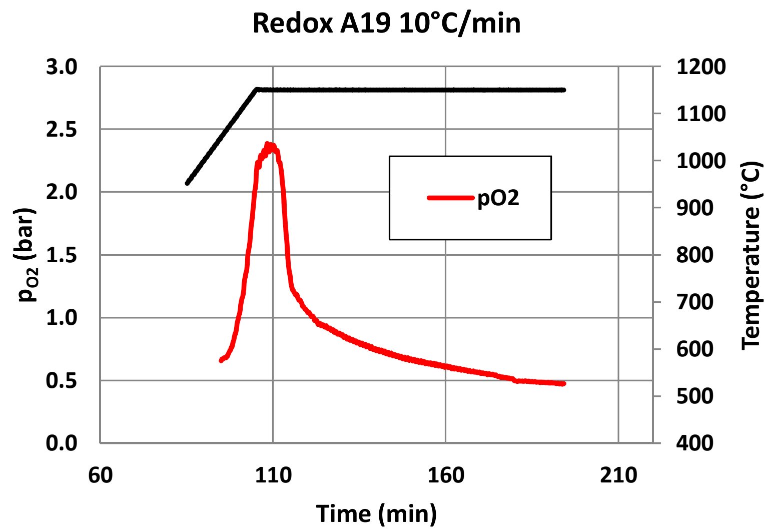
Summary of HLW Melt and Glass Constraints

Constraint Description	Value/Range
Product Consistency Test (PCT) normalized B release	$rB < 16.70$ (g/L)
PCT normalized Li release	$rLi < 9.57$ (g/L)
PCT normalized Na release	$rNa < 13.35$ (g/L)
Nepheline rule	$gSiO_2/(gAl2O3 + gNa_2O + gSiO_2) \geq 0.62$
CdO concentration in glass or Toxicity Characteristic Leaching Procedure (TCLP) Cd concentration	$gCdO \leq 0.1$ (wt%) or $cCd < 0.48$ (mg/L)
Tl_2O concentration in glass	$gTl2O \leq 0.465$ (wt%)
Temperature at 1 vol% crystal	$T1\% \leq 950$ (°C)
Non spinel phase rule	$gAl_2O_3 + gThO_2 + gZrO_2 < 18$ (wt%) $gThO_2 + gZrO_2 < 13$ (wt%) $gZrO_2 < 9.5$ (wt%)
Viscosity at 1150°C	20 (P) $\leq \eta1150 \leq$ 80 (P)
Viscosity at 1100°C	$\eta1100 \leq 150$ (P)[a]
Electrical conductivity at 1100°C	0.1 (S/cm) $\leq \varepsilon1100$
Electrical conductivity at 1200°C	$\varepsilon1200 \leq 0.7$ (S/cm)
SO_3 concentration in glass (target)[b]	$gSO_3 \leq 0.44$ (wt%)

(a) Note that the lower limit of 10 Poise on η1100 is unnecessary given the lower limit of 20 Poise on η1150. This is because viscosity decreases with increasing temperature.
(b) The concentration before applying retention factors to account for losses during vitrification process is used. For all other constraints, the concentration values obtained after applying retention factors are used.

EGA and O_2 partial pressure by RAPIDOX



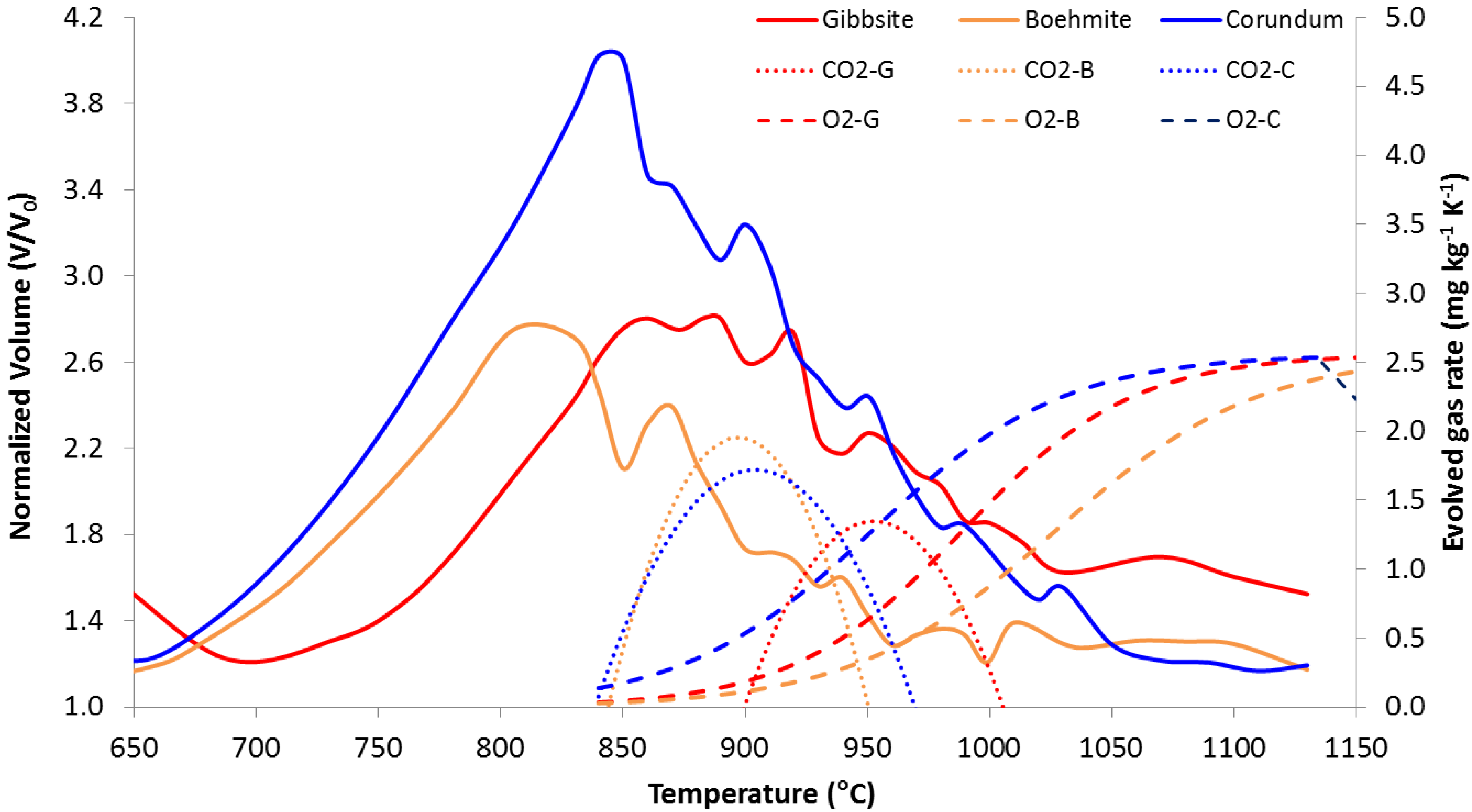


The evolved gas analysis, and the Rapidox analysis of pO_2 during the melting of A19 feed.

The black solid lines in both graphs show the temperature profile.

The melt is highly oversaturated with oxygen. Such a high oversaturation is not likely to arise solely from the iron redox equilibrium, but also from the oxygen "stored" in the feed from earlier batch decomposition reactions (mostly nitrates).

Foaming Curve & Secondary Foam

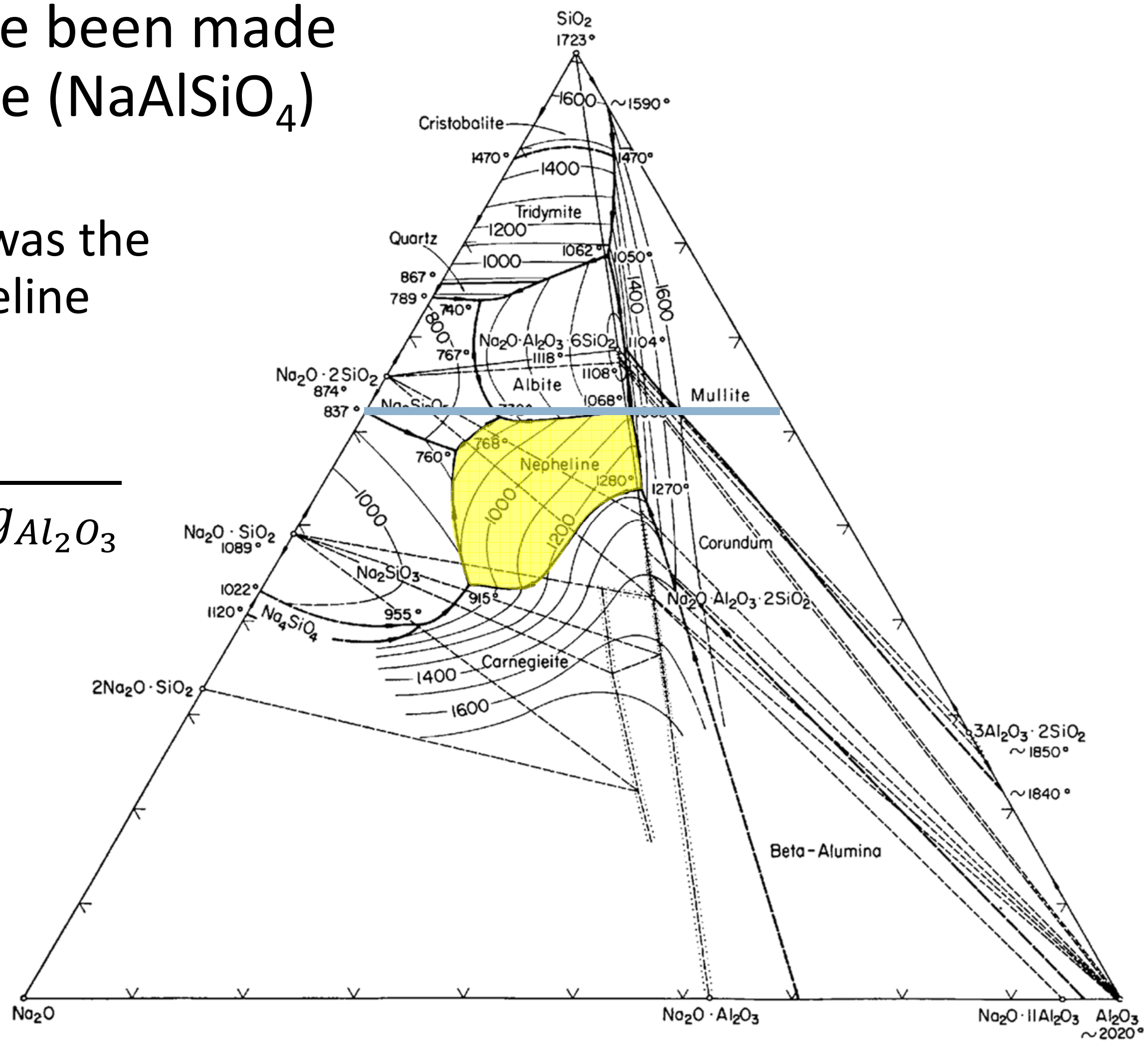


- Detected CO_2 gas in the foam layer was a residual gas remaining from the feed reaction and involved in the primary foam.
- Following detected O_2 gas was from iron redox reaction and involved in the secondary foam.

Nepheline Precipitation

- Many attempts have been made to predict Nepheline ($NaAlSiO_4$) formation
  - the most successful was the Li et al. 1997[13] Nepheline discriminator:

$$ND = \frac{g_{SiO_2}}{g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}}$$



Foaming in High Bi-P HLW Glass Melts

Glass melts with high loadings of Bi-P wastes were found to exhibit foaming of the melt during cooling

- Potential risk of overflow during HLW canister cooling

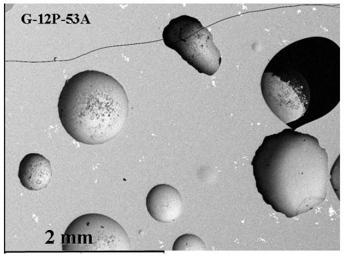
Testing was performed to determine the foaming mechanism

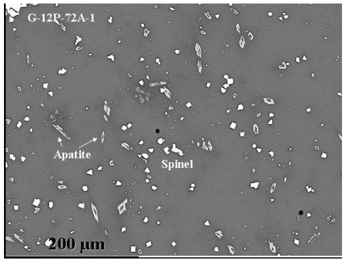
- Stabilization of hexavalent Cr in phospho-chromate environments in the melt; auto-reduction to trivalent Cr on cooling as a result of its higher stability in spinels

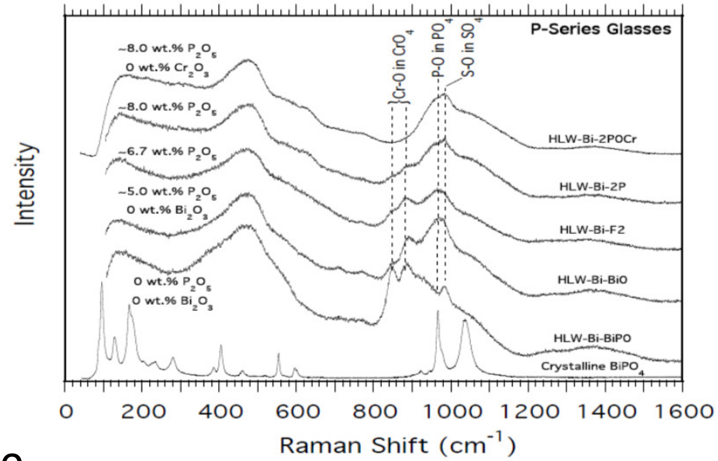
Results were used to modify glass formulations to mitigate melt foaming

- Increased Al content to compete with Cr in phosphorus environments

Confirmed in one-third scale DM1200 pilot melter tests



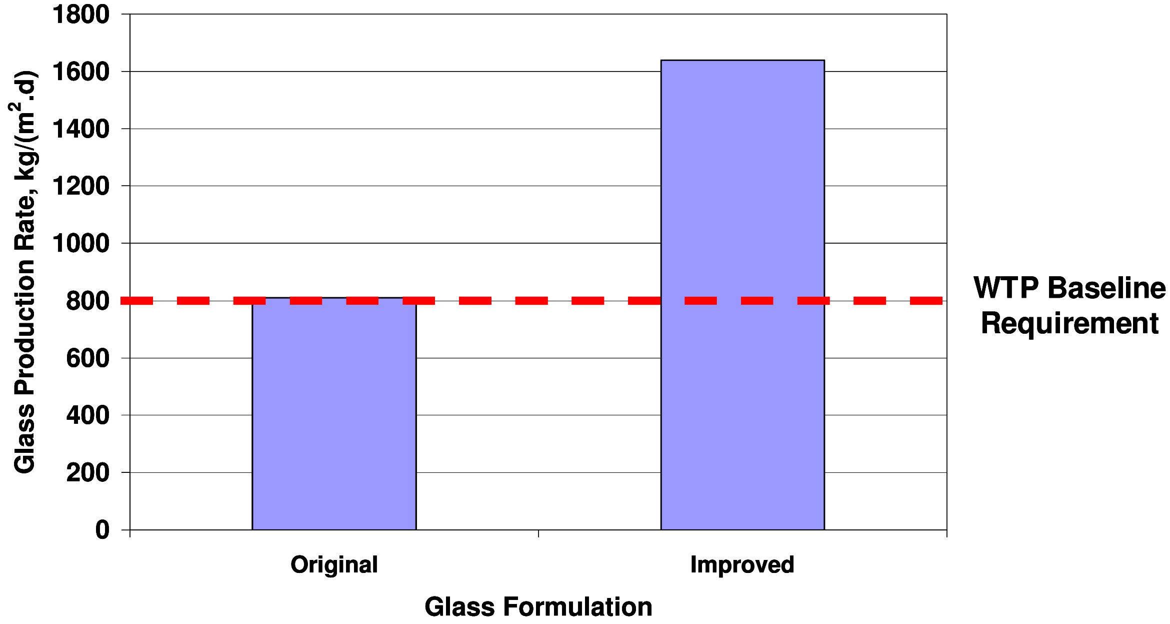




VSL-07R1010-1, Rev. 0; VSL-10R1780-1, Rev.0

Melt Rate and Waste Loading in High Bi-P HLW Glasses

- Glass formulations developed with very high waste loading (50 wt% waste oxides) for high Bi-P HLW streams
- However, slow melt rates were observed in scaled melter tests
- Melt rate screening tests were used to develop improved formulations with increased melt rate while retaining the same high waste loadings



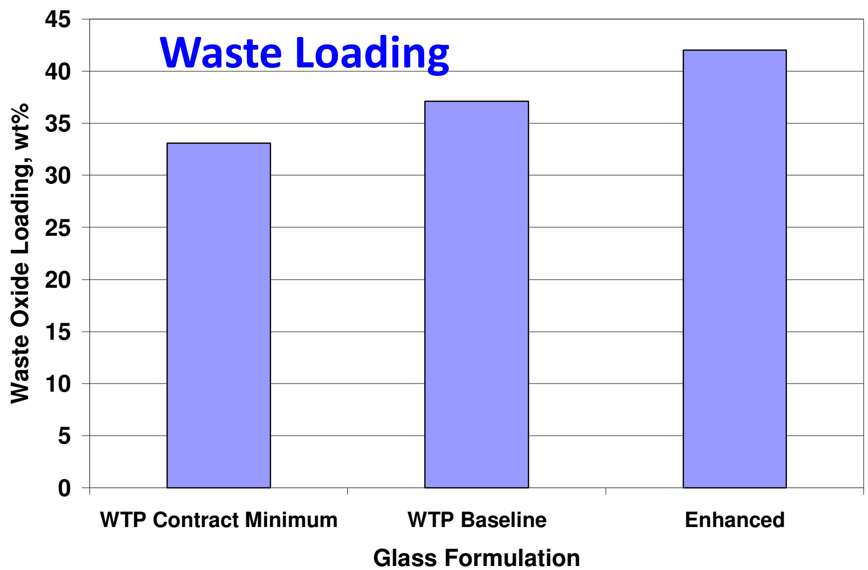
VSL-07R1010-1, Rev. 0; VSL-10R1780-1, Rev.0; VSL-12T2770-1, Rev. 0

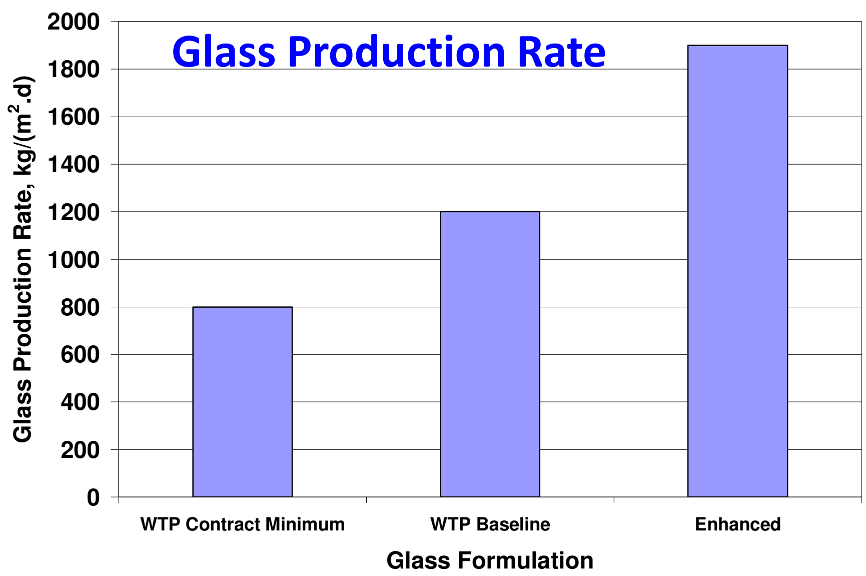
Melt Rate and Waste Loading in High Fe HLW Glasses

Waste loading in typical high-Fe HLW stream is limited by spinel crystallization

Higher waste loadings often result in lower processing rates

Improved formulations have been developed with both high melt rates and high waste loadings

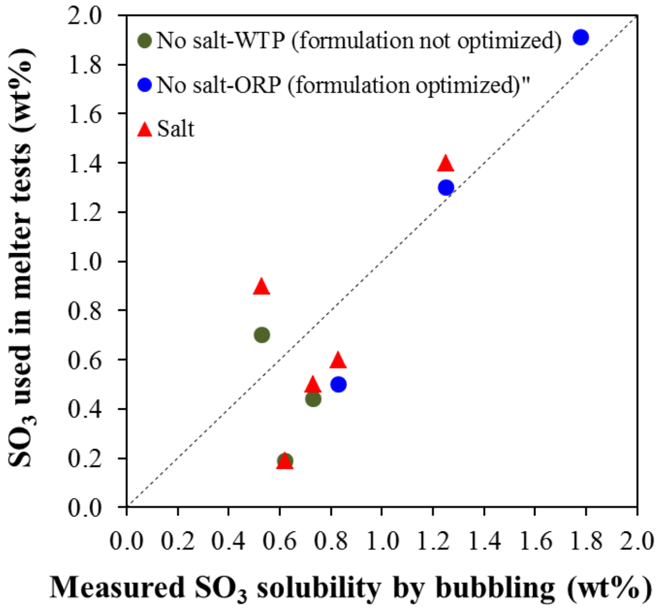


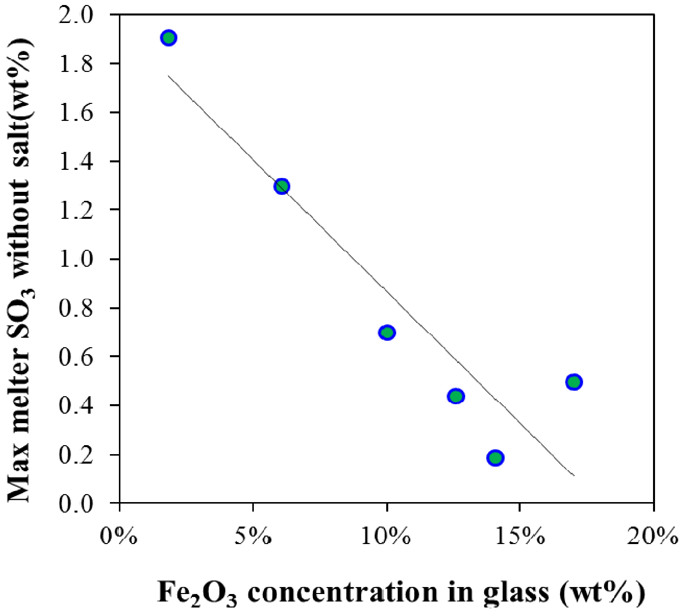


VSL-12R2490-1, Rev. 0

Sulfur Tolerance in HLW Glass

- At concentrations above the sulfur tolerance limit, a sulfate containing salt accumulates on the melt surface
- Limited melter tests suggest that sulfur tolerance is related to both Fe_2O_3 concentration and measured solubility in crucible melts





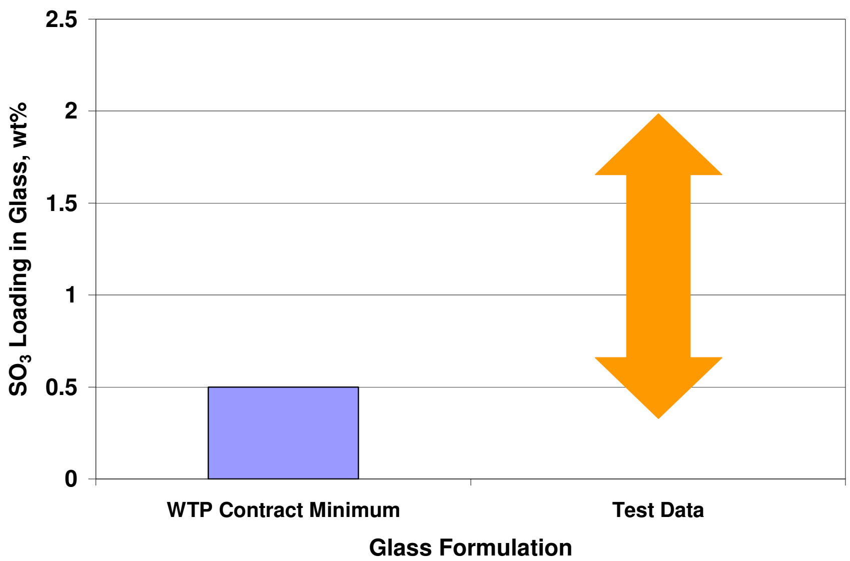
Waste Loading in High Sulfur HLW Glasses

About 22% of the projected HLW feed batches to the WTP are expected to be limited by sulfate

The sulfate content in the HLW fraction is dependent on the washing performance in pretreatment

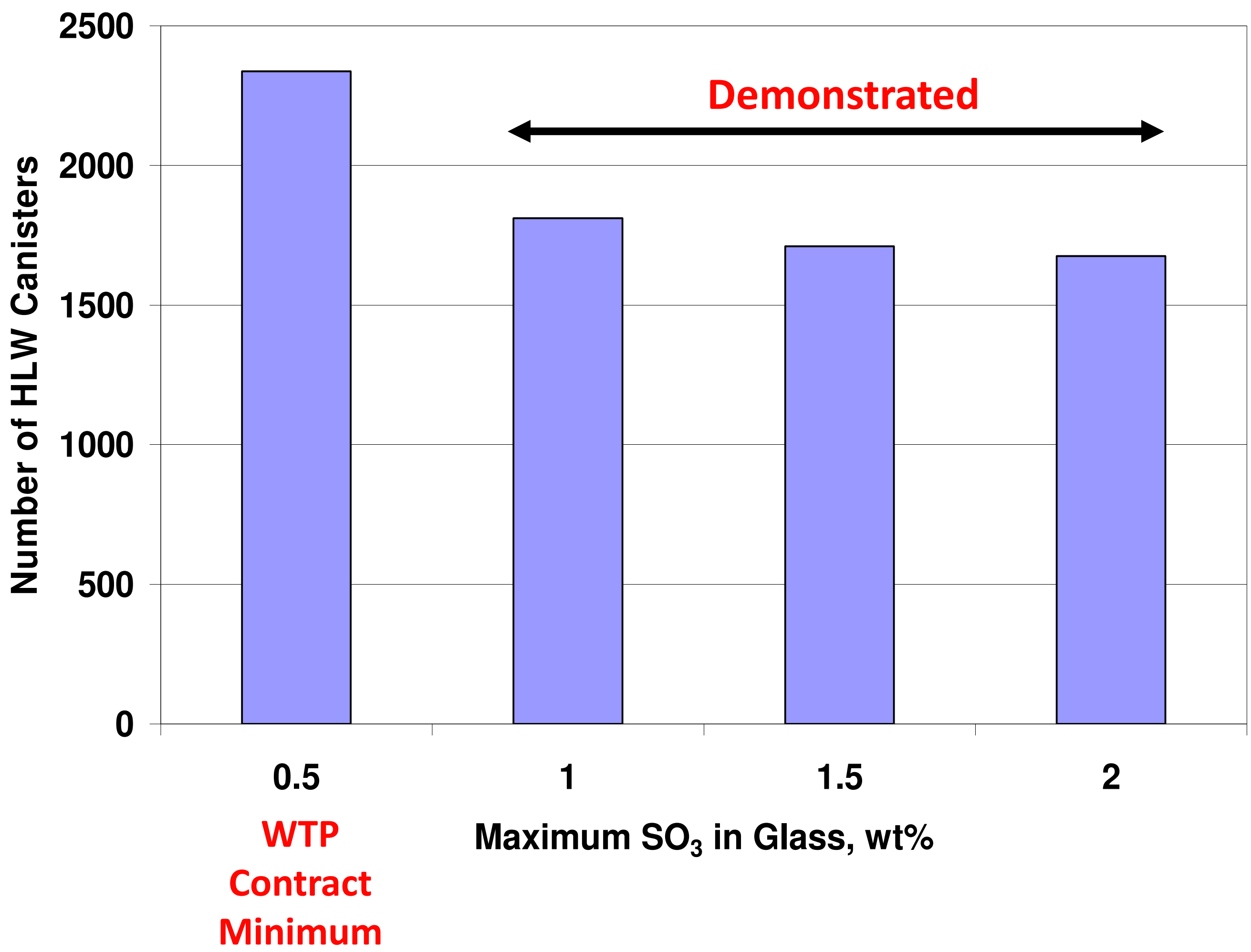
High sulfate feeds pose the risk of molten salt formation in the melter

HLW glass formulations with high sulfate solubility have been developed to address this risk



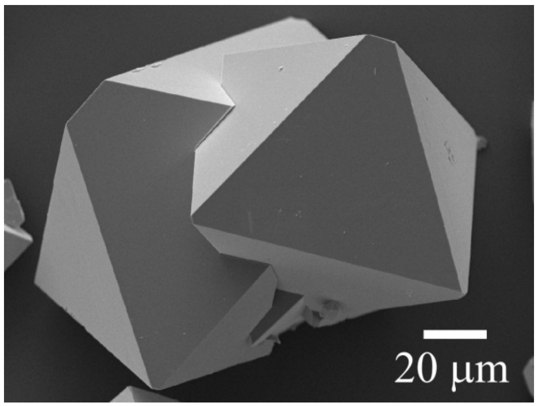
VSL-12R2540-1, Rev. 0

Effect of Glass Sulfate Capacity on Amount of Sulfate-Limited HLW Glass

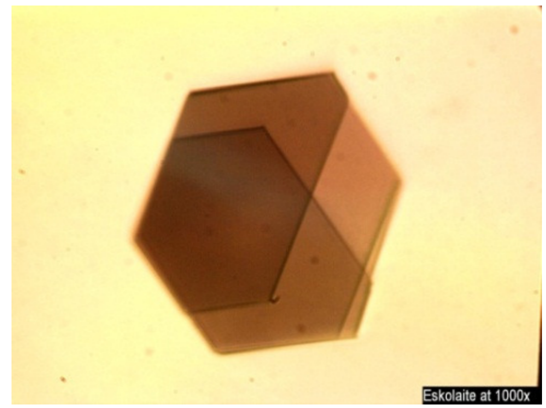


Crystal Tolerance

Spinel [Fe,Zn,Mn][Fe,Cr,Mn,Al]$_2$O$_4$



Eskolaite Cr_2O_3



- Two approaches considered
  1. Matyas et al. 2013[4] model for predicting the accumulation rate of spinel in the pour-spout riser at 850°C
  2. Limit the crystal fraction in the melt